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AIR VEHICLE TECHNOLOGY INTEGRATION PROGRAM (AVTIP)

Delivery Order 0033: Advanced Sol-Gel Adhesion Processes - Transition Support

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THIS TECHNICAL REPORT IS APPROVED FOR PUBLICATION.

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This report summarizes optimization and transition support work for surface preparations utilizing nanostructured sol-gel coatings on metal alloy substrates. The project focuses on optimization and transition of user-friendly sol-gel methods for preparing metal surfaces for bonding with 250°F-cure epoxy adhesives. Studies indicate that careful choice of abrasive media and tools is required to achieve reproducible performance for the surface preparation of aluminum alloys. Verification of these processes and expansion of the processing guidelines were determined under this effort. Transition of materials and processing information and support of transition efforts to specific customers was provided throughout the effort. Procedures were documented specifying all of the preferred materials and processes.

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Table of Contents

List of Figures

List of Tables

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The Boeing Company is pleased to be part of a Tri-Services/Industry working team developing technology under the Environmental Security Technology Certification Program Project PP-0204, “Demonstration/Validation of Sol-Gel Surface Preparation for Metal Adhesive Bonding.” The Boeing Company leads the sol-gel development and technical integration associated with this effort under Air Force contract F33615-00-D-3052, Delivery Order 0033. This report encompasses work performed between 6/21/02 and 7/15/05.

We would like to acknowledge our ESTCP Team members and our colleagues from Boeing Commercial Airplanes for collaborative discussions and contributions to the overall effort.

1 Executive Summary

This report summarizes optimization and transition support work for surface preparations utilizing nanostructured sol-gel coatings on metal alloy substrates. The project focused on optimization and transition of user-friendly sol-gel methods for preparing metal surfaces for bonding with 250°F-cure and 350°F-cure epoxy adhesives.

In order to facilitate the smooth transition of these processes into production and repair shops, several studies were undertaken to improve the robustness of the process and verify the recommended techniques would provide adequate performance and durability.

Several areas were investigated: deoxidation and surface preparation methods; primer curing methods, compatibility with typical adhesive systems, and sol-gel kitting and packaging methods.

Studies indicate careful choice of abrasive media and tools is required to achieve reproducible performance for the surface preparation of aluminum alloys. Verification of these processes and expansion of the processing guidelines were determined under this effort. An abrasive paper was identified that gives reproducible performance under a variety of conditions. This paper and process was included in baseline procedures. Second source abrasive papers were identified and their performance continues to be verified. The same abrasives may also be used effectively on titanium alloy substrates.

Alternatively, chemical deoxidation methods that give good performance were identified for parts and hardware that cannot use abrasive methods. The best performing methods on aluminum used a mild alkaline conditioner with or without an additional acid desmut. The use of an open air plasma process may improve the surface cleanliness, but the results were not conclusive.

Minimum cure times and temperatures were identified for parts that cannot tolerate an extensive heat-cure cycle. Data indicate a minimum of 200°F was necessary to reproducibly cure the primer under vacuum bag conditions. Cocuring of the primer with different adhesive systems was evaluated to determine the compatibility of the primer with the adhesive chemistries. Significant differences could be seen between adhesives. Commercially available low-volatile organic compound (VOC) bond primers were evaluated for use with the sol-gel coating system. Careful selection and testing of these bond primers must be conducted with the sol-gel system to ensure compatibility and durability in a hot/wet environment.

Extensive kitting and packaging evaluations resulted in a packaging system that showed the durability and resistance to storage conditions required for use in a production and repair setting.

Transition of materials and processing information and support of transition efforts to specific customers were provided throughout the effort. Procedures were documented specifying all of the preferred materials and processes and performance data.

2 Introduction

2.1 Background

This work is part of a Tri-Services team effort funded in part by the Environmental Security Technology Certification Program (ESTCP) under Project #PP-0204, "Demonstration/Validation of Sol-Gel Surface Preparation for Metal Adhesive Bonding". PP-0204 is the technology validation and demonstration phase and follow-on effort from a Strategic Environmental Research and Development Program (SERDP) funded project that developed prebond surface preparations and hybrid primers utilizing sol-gel technology on aluminum, titanium, and steel substrates. Previous work has been documented and released in various technical reports[1].

The ESTCP project focuses on the optimization, validation, and demonstration of user-friendly sol-gel methods for preparing metal surfaces for bonding with 250°F-cure and 350°F-cure epoxy adhesives. The goals of the project are to design processes that 1) use environmentally-friendly materials, 2) increase durability, 3) improve process robustness, 4) decrease repair time, 5) use simple equipment and procedures, and 6) increase affordability. Depot sites, including Naval Air Depot (NADEP)-North Island, NADEP-Cherry Point, NADEP-Jacksonville, Warner Robins Air Logistics Center (ALC), and Corpus Christi Army Depot (CCAD) were involved in the requirements generation and testing cycle to ensure end-user needs are being met and technology transition issues were assessed.

This report summarizes Boeing's portion of the team effort. It covers work developing robust surface preparation methods and techniques, optimization of abrasion methods and sandpaper variables, developing durable kitting procedures and packaging, devising quality control and validation methods, validation of kitting shelf-life, validation of processes for depot use, and support of transition activities.

2.1.1 Surface Treatments

Aircraft repair manuals or technical orders typically require the use of surface preparations such as tankline phosphoric acid anodize (PAA), manual PAA (phosphoric acid containment system (PACS) or phosphoric acid non-tank anodize (PANTA))[2], hydrofluoric acid (HF)/Alodine®, or acid paste etches for the repair of aluminum alloy structure. These surface preparations rely on hazardous acids and/or time-consuming and complex processing steps. Lack of process robustness results in some bonding repair practices that do not consistently yield the expected bond performance. The phosphoric acid in PAA and sulfuric acid used in common paste acid etches (such as Pasa-Jell), are difficult to contain and rinse off when conducting on-aircraft repairs of complex shapes and assemblies. The HF in HF/Alodine® is a health hazard.

A grit-blast/silane surface preparation has been employed in many military repairs. It provides an alternative to the use of acids, but requires a grit-blasting step, elevated-temperature drying, and several hours to perform[3]. The grit-blast pretreatment method is also less desirable for repair applications due to concerns regarding containment of the material in a field or depot setting. The sol-gel process is similar to the silane surface preparations currently used, but it has a

number of advantages. It is quicker, eliminates the elevated-temperature drying step, and can eliminate the grit-blasting step in many applications.

The sol-gel process tested here involves the use of the Boeing-developed Boegel-EPII formulation, which is currently commercially available as AC-130 from Advanced Chemistry and Technology (Garden Grove, CA, www.actechaero.com). This aqueous-based sol-gel solution can be brushed, sprayed, or swabbed onto the surface to be treated and does not require rinsing.

The sol-gel surface preparation process works by producing a nanostructured gradient interphase coating. One side is molecularly bonded to the oxide structure on the metal and the other side is molecularly crosslinked with the adhesive primer, Figure 2.1-1. The type of bonding at the metal interface determines the long-term durability of the system. For high-performance durable bonding the metal alloy surface must be scrupulously clean and have an active metal oxide surface chemistry. Contamination on the surface can reduce the number of surface reactive sites and subsequently reduce the surface density of bonds with the sol-gel coating. This will reduce the ultimate durability of the system.

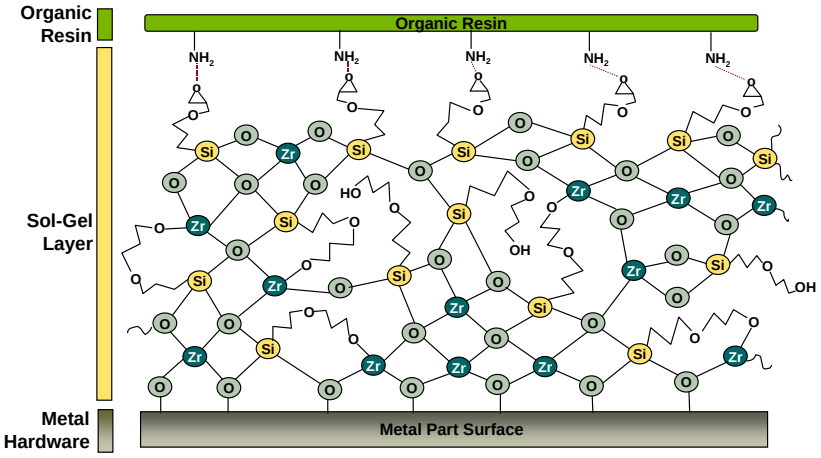


Figure 2.1-1 Notional schematic of sol-gel adhesion-promoting coating on a metal part

Certain pretreatment methods provide a better surface for accepting the sol-gel coating and forming a permanent chemical bond. For example, specific pretreatment methods on titanium which increase the population of hydroxyl groups per unit area on the surface provide long-term durability under hot/wet conditions. On aluminum and titanium alloys, large differences in performance were found as a result of different "sandpapers" or abrasive papers used during the deoxidation step. The rationale was not completely straightforward. Favored sandpapers did two things in general: 1) they provided a more efficient method of deoxidation, removing metal oxides without dragging materials from the intermetallic regions across the surface and 2) they did not leave an organic residue smear on the surface which interferes with the subsequent coating reaction process. These details are described in subsequent sections.

3 Experimental Procedures

3.1 Materials

3.1.1 General

This program examined the use of the sol-gel surface treatments on metal alloy systems. Testing was conducted on various alloys, including 2024-T3, Clad-2024-T3, 7075-T6, Ti-6Al-4V, and stainless 301, 304, and AM355. Unless otherwise noted, testing was conducted in a laboratory setting under ambient temperature and humidity conditions. No specific control of the environmental conditions in the laboratory was accounted for during this testing.

An example of a typical pretreatment process using standard manual deoxidation procedures is outlined in Table 3.1-1 to bond metal alloy test specimens.

Table 3.1-1 Manual Deoxidation Process Method Used to Prepare Sol-Gel Test Specimens

Step #	Process
1	Solvent wipe with methyl ethyl ketone (MEK) followed by acetone until cheesecloth is clean.
2	Abrade using a random orbital sander or die grinder equipped with preferred sandpaper(s).
3	Blow off loose particles with clean dry air.
4	Spray surfaces with Boegel-EPII (AC-130) for 2-3 minutes, keeping surfaces wet. Apply sol-gel within 30 minutes of the abrasion process.
5	Dry at ambient temperature for one hour.
6	Spray-apply adhesive bond primer, Cytec BR 6747-1 (0.00015 – 0.00040”-thick).
7	Heat cure primer at 250°F +/- 10°F for 75 minutes.
8	Apply adhesive, AF 163-2M.
9	Cure at 250°F in autoclave at 45 psig (90 minutes).

3.1.2 Manual Deoxidation Materials and Equipment

The sanding process was typically carried out using a random orbital sander or a die grinder. Air powered tools were fitted with a filtered rear exhaust. The tools used in these studies are shown in Table 3.1-2.

Table 3.1-2 Surface Preparation Tool Details for Sandpaper Variation Study

Surface Prep Tools	Manufacturer	Abrasive diameter	Speed
Random Orbital Sander	Dewalt	5 inch	10,500 orbits/minute
Die Grinder	Myton	3 inch with 3-inch backing pad	20,000 rpm

The abrasion process involved sanding with the candidate abrasive paper or pad for one to two minutes over approximately 6 in x 6 in sections. To ensure complete coverage, the sander was guided from side to side across the entire 6 in x 6 in area then moved in a perpendicular direction to achieve one crosscoat. The sandpaper was changed when it became worn, as evidenced by

tears, seizing of the tool, and clogging. At a minimum, two fresh pieces of sandpaper for each 6 in x 6 in area was used. The sanding speed was adjusted in particular experiments and tended to range from a one to two minute period over a 6 in x 6 in area.

Figure 3.1-1 summarizes the abrasion procedure.

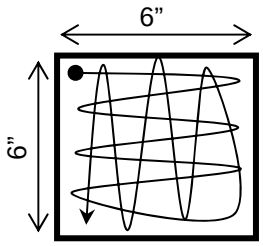
Area/Sanding Pattern	
Sandpaper Changeout	1 piece/36 in^2
Time Sandpaper Used	1-2 min/36 in^2

Figure 3.1-1 Abrasion process summary

After completion of the sanding procedure, loose grit was removed from the surface of the specimen using clean, dry compressed air or nitrogen. No wiping of the surface, either dry or with solvent, was carried out in any of the testing, unless otherwise noted. For standard experiments, the specimens were coated with the sol-gel solution within 30 minutes of the abrasion process.

3.1.3 Sol-Gel Chemistries

A version of the waterborne silicon-zirconium sol-gel system designated for use with epoxy adhesive systems, Boegel-EPII, was tested throughout this program. Changes to the formulation and application chemistry were carried out as noted in the sections of this document.

The sol-gel solution was either spray-applied or brush-applied on the surface of the specimens, which were typically positioned vertically on a spray rack. The solution was reapplied several times, keeping the surface wet for a period of two minutes. Sol-gel application was generally carried out using spray equipment such as a high volume, low pressure (HVLP) spray gun, a manual pump spray apparatus, or a clean, natural bristle brush. The specimens were allowed to drain and dry for a minimum of 60 minutes under ambient conditions before an adhesive primer was applied. In all cases where bond primer was applied, the adhesive primer was applied within 24 hours of sol-gel application.

3.1.4 Primers and Adhesives

Cytec Fiberite BR 6747-1 adhesive bond primer was chosen as the baseline bond primer for testing in this program. The primer was spray-applied to the surface using an HVLP gun to a dry film thickness of 0.15 – 0.40 mil (0.00015 – 0.0004 in). The primer was cured at 250°F (+/- 10°F) for 60-90 minutes per the Boeing BMS5-89[4] specification.

For 250°F-cure film adhesive (BMS5-101[5]) testing, specimens were bonded with 0.06 psf AF 163-2M film adhesive from 3M Company, unless otherwise noted. The adhesive was cured for 90 minutes at 250°F (+/- 10°F) and 35-40 psi in an autoclave, unless otherwise noted.

3.2 Testing

3.2.1 Performance and Durability Testing

The primary screening test used in this program intended to assess the long-term environmental durability of the bonded joints is the wedge test (ASTM D 3762).[6] Treated adherends, sized 6 in x 6 in, were bonded together, and the panels were machined into 1-in wide specimens. The thickness of the panels used in the screening studies was a function of the alloy used. Typically for aluminum alloys, the nominal sheetstock thickness used was 0.125 in. A wedge was inserted into one end of the specimen bondline, and the resultant crack generated within the adhesive was measured. The sample was placed in a hot/wet environment and the crack length was measured periodically. For screening purposes, bonds exhibiting at least 95% cohesive failure within the adhesive with minimal crack growth after 28 days were considered acceptable.

The environmental conditions utilized were 140°F and >98% relative humidity (RH). The crack growths and failure modes of the specimens were used to calculate the significance of each factor tested. Successful wedge test specimens with optimum processing conditions exhibited crack growths of less than 0.25 inch with cohesive failure modes (within the adhesive layer). Small “nicks” of interfacial failure or “adhesive failure” (at the metal interface) were sometimes detected at the edges of these specimens. It was estimated that the area of these small nicks was roughly 5% or less of the specimen test area. Failure modes for all developmental specimens were reported in conjunction with the wedge crack extension data.

Additional screening utilized tensile lap shear per ASTM D 1002[7] as well as climbing drum peel testing per Boeing specification BSS7206[8], floating roller peel testing to both BSS7206 and ASTM D3167[9] and double cantilever beam (DCB) testing per Boeing specification BSS7208.[10]

4 Results and Discussion

4.1 Deoxidation Studies

4.1.1 Aluminum Chemical Deoxidation Optimization

A test series was conducted to determine optimal deoxidation methods for yielding maximum durability on aluminum substrates. The goal was to develop a nonabrasive (chemical) method to deoxidize the surface of aluminum, for hardware where abrasion is not a possibility. The test matrix is shown in Table 4.1-1.

Table 4.1-1 Aluminum Deoxidation Matrix Study

Specimen Number	Alloy	Deox Method
030318-jwg-1A	2024	Amchem 6-16
030318-jwg-1B	7075	
030318-jwg-2A	2024	Deoxalume 2300
030318-jwg-2B	7075	
030318-jwg-3A	2024	Amchem 6-16 / Isoprep 44 alkaline clean (conditioner)
030318-jwg-3B	7075	
030318-jwg-4A	2024	Isoprep 177 etch / Amchem 6-16 desmut
030318-jwg-4B	7075	
030318-jwg-5A	2024	Isoprep 177 etch / no desmut
030318-jwg-5B	7075	
030318-jwg-6A	2024	Grit-blast
030318-jwg-6B	7075	

Wedge test and climbing drum peel specimens were made to assess the various differences in surface chemistry provided by the different deoxidizers. Specimens prepared by grit-blasting with #180 grit alumina were included to act as controls. Wedge testing was conducted at 140°F and greater than 98% RH. Climbing drum peel tests were conducted at ambient temperature conditions (approximately 72°F and 50% RH). Climbing drum peel test results are shown in Table 4.1-2 and Figure 4.1-1.

Both standard chromated deoxidizers and nonchromated deoxidizers were included in this study. Also, the effects of alkaline etching and desmutting were assessed. The results show significant differences in the performance and durability of the sol-gel system with the different deoxidizers.

Peel strength test results did not show any great differences in the deoxidation procedures and were comparable to the grit-blast controls, with the exception of specimen 5B (Isoprep 177, no desmut). The failure mode for specimen 5B appears to be within the smut layer of the etched 7075 aluminum. Specimen 5A, which was 2024 aluminum, failed cohesively within the adhesive. It was noted during the deoxidation procedure that the smut layer on the 7075 aluminum appeared to be darker and in greater amount than what was observed on the 2024 aluminum.

Wedge test exposure data are shown in Table 4.1-3 and Figure 4.1-2 and Figure 4.1-3.

Table 4.1-2 Aluminum Deoxidation Matrix Study: Peel Test Results

Spec. No.	Alloy / Deox Method	Peel Strength	St. Dev.
1A-1	2024 / Amchem 6-16	87.4	
1A-2		82.1	
1A-3		82.2	
1A-avg		83.9	3.0
1B-1	7075 / Amchem 6-16	76.7	
1B-2		64.5	
1B-3		63.2	
1B-avg		68.1	7.4
2A-1	2024 / Deoxalume 2300	86.0	
2A-2		77.9	
2A-3		80.8	
2A-avg		81.6	4.1
2B-1	7075 / Deoxalume 2300	66.1	
2B-2		57.4	
2B-3		57.8	
2B-avg		60.4	4.9
3A-1	2024 / Amchem 6-16 / Isoprep 44	84.1	
3A-2		79.8	
3A-3		82.7	
3A-avg		82.2	2.2
3B-1	7075 / Amchem 6-16 / Isoprep 44	69.4	
3B-2		67.1	
3B-3		71.5	
3B-avg		69.3	2.2

Spec. No.	Alloy / Deox Method	Peel Strength	St. Dev.	Failure % Cohesive
4A-1	2024 / Isoprep 177 / Amchem 6-16	82.8		100
4A-2		79.8		100
4A-3		77.1		100
4A-avg		79.9	2.9	100
4B-1	7075 / Isoprep 177 / Amchem 6-16	71.2		100
4B-2		63.7		100
4B-3		66.7		100
4B-avg		67.2	3.8	100
5A-1	2024 / Isoprep 177 / no desmut	83.8		100
5A-2		81.0		100
5A-3		86.6		100
5A-avg		83.8	2.8	100
5B-1	7075 / Isoprep 177 / no desmut	5.4		100
5B-2		5.4		100
5B-3		5.4		100
5B-avg		5.4	0.0	100
6A-1	2024 / grit-blast	92.8		100
6A-2		83.0		100
6A-3		83.3		100
6A-avg		86.4	5.6	100
6B-1	7075 / grit-blast	68.3		100
6B-2		64.2		100
6B-3		65.5		100
6B-avg		66.0	2.1	100

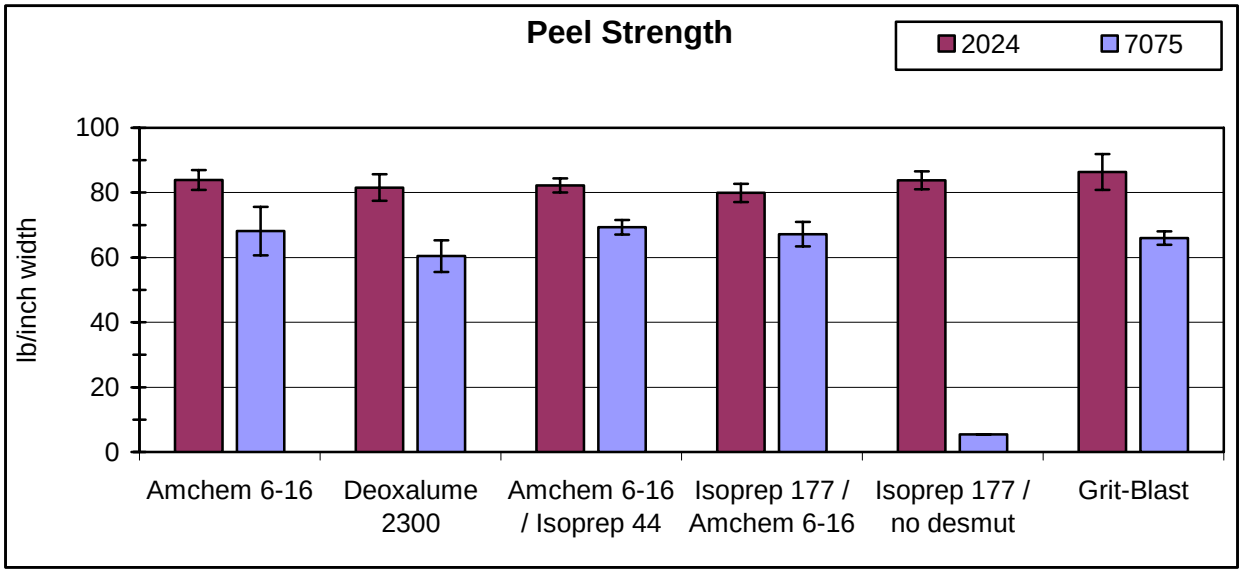


Figure 4.1-1 Peel strength data for variations in aluminum deoxidizers

Table 4.1-3 Wedge Test Data for Variations in Aluminum Deoxidizers

Spec. No.	Alloy / Deox Method	Crack length (inch) after Exposure to 140°F & >98% RH (hours)						Total Crack Growth	Std Dev Crack Growth	Percent Cohesive Failure	Comments
		0	24	168	336	504	672				
1A-1	2024 / Amchem 6-16	1.10	1.22	1.25	1.32	1.32	1.36	0.26		90	Adhesive failures were limited to areas within 0.1 inch from the edges.
1A-2		1.12	1.18	1.23	1.32	1.32	1.32	0.20		92	
1A-3		1.12	1.24	1.31	1.40	1.40	1.40	0.28		93	
1A-4		1.11	1.27	1.27	1.42	1.42	1.42	0.31		93	
1A-5		1.25	1.35	1.35	1.46	1.46	1.46	0.21		93	
1A-avg		1.14	1.25	1.28	1.38	1.38	1.39	0.25	0.05	92	
1B-1	7075 / Amchem 6-16	1.26	1.36	1.36	1.43	1.43	1.43	0.17		90	Adhesive failures were limited to areas within 0.2 inch from the edges.
1B-2		1.16	1.27	1.27	1.42	1.42	1.42	0.26		90	
1B-3		1.27	1.27	1.40	1.45	1.45	1.45	0.18		92	
1B-4		1.25	1.33	1.33	1.46	1.46	1.46	0.21		92	
1B-5		1.32	1.40	1.46	1.55	1.55	1.55	0.23		89	
1B-avg		1.25	1.33	1.36	1.46	1.46	1.46	0.21	0.04	91	
2A-1	2024 / Deoxalume 2300	1.26	1.38	1.55	1.80	1.91	1.91	0.65		7	Finger one was a massive adhesive failure. Other fingers were limited to areas within 0.3 inches from the edges.
2A-2		1.15	1.29	1.31	1.41	1.41	1.41	0.26		77	
2A-3		1.18	1.26	1.26	1.36	1.36	1.36	0.18		80	
2A-4		1.17	1.25	1.30	1.38	1.38	1.38	0.21		76	
2A-5		1.24	1.38	1.38	1.51	1.51	1.51	0.27		84	
2A-avg		1.20	1.31	1.36	1.49	1.51	1.51	0.31	0.19	65	
2B-1	7075 / Deoxalume 2300	1.25	1.37	1.65	1.87	1.87	1.98	0.73		0	Complete adhesive failure.
2B-2		1.22	1.32	1.58	1.80	1.89	1.89	0.67		0	
2B-3		1.32	1.44	1.44	1.60	1.79	1.79	0.47		0	
2B-4		1.29	1.39	1.68	1.91	1.91	1.91	0.62		0	
2B-5		1.30	1.40	1.73	1.94	1.94	1.94	0.64		0	
2B-avg		1.28	1.38	1.62	1.82	1.88	1.90	0.63	0.10	0	
3A-1	2024 / Amchem 6-16 / Isoprep 44	1.12	1.16	1.16	1.24	1.24	1.24	0.12		99	Adhesive failures were limited to areas less than 0.05 inch from the edges.
3A-2		1.17	1.20	1.20	1.26	1.26	1.26	0.09		99	
3A-3		1.20	1.2.5	1.25	1.28	1.28	1.28	0.08		99	
3A-4		1.30	1.36	1.36	1.36	1.36	1.36	0.06		99	
3A-5		1.26	1.29	1.29	1.29	1.29	1.29	0.03		100	
3A-avg		1.21	1.25	1.25	1.29	1.29	1.29	0.08	0.03	99	
3B-1	7075 / Amchem 6-16 / Isoprep 44	1.27	1.27	1.27	1.41	1.41	1.41	0.14		97	Adhesive failures were limited to areas less than 0.1 inch from the edges.
3B-2		1.15	1.15	1.20	1.35	1.35	1.35	0.20		97	
3B-3		1.17	1.17	1.17	1.32	1.32	1.32	0.15		97	
3B-4		1.22	1.22	1.26	1.37	1.37	1.37	0.15		97	
3B-5		1.26	1.31	1.31	1.39	1.39	1.39	0.13		99	
3B-avg		1.21	1.22	1.24	1.37	1.37	1.37	0.15	0.03	97	

Table 4.1-3 Wedge Test Data for Variations in Aluminum Deoxidizers (cont'd)

Spec. No.	Alloy / Deox Method	Crack length (inch) after Exposure to 140°F & >98% RH (hours)						Total Crack Growth	Std Dev Crack Growth	Percent Cohesive Failure	Comments
		0	24	168	336	504	672				
4A-1	2024 / Isoprep 177 / Amchem 6-16	1.21	1.26	1.26	1.42	1.42	1.42	0.21		97	Adhesive failures were limited to areas less than 0.1 inch from the edges.
4A-2		1.18	1.24	1.24	1.38	1.38	1.38	0.20		97	
4A-3		1.12	1.12	1.12	1.27	1.27	1.27	0.15		97	
4A-4		1.12	1.12	1.12	1.27	1.27	1.27	0.15		97	
4A-5		1.18	1.28	1.28	1.35	1.35	1.35	0.17		97	
4A-avg		1.16	1.20	1.20	1.34	1.34	1.34	0.18	0.03	97	
4B-1	7075 / Isoprep 177 / Amchem 6-16	1.32	1.36	1.36	1.50	1.50	1.50	0.18		97	Adhesive failures were limited to areas less than 0.1 inch from the edges.
4B-2		1.30	1.30	1.30	1.43	1.43	1.43	0.13		92	
4B-3		1.32	1.32	1.32	1.46	1.46	1.46	0.14		98	
4B-4		1.41	1.48	1.48	1.48	1.48	1.48	0.07		96	
4B-5		1.32	1.42	1.42	1.54	1.54	1.54	0.22		96	
4B-avg		1.33	1.38	1.38	1.48	1.48	1.48	0.15	0.06	96	
5A-1	2024 / Isoprep 177 / no desmut	1.27	1.48	1.53	1.64	1.64	1.64	0.37		10	Most failures started out adhesive and switched to cohesive as the crack progressed. There were adhesive failures beyond the crack tip (from breaking apart the wedges).
5A-2		1.23	1.38	1.43	1.55	1.55	1.55	0.32		13	
5A-3		1.20	1.32	1.32	1.46	1.46	1.46	0.26		50	
5A-4		1.25	1.34	1.34	1.48	1.48	1.48	0.23		57	
5A-5		1.32	1.42	1.46	1.58	1.58	1.58	0.26		38	
5A-avg		1.25	1.39	1.42	1.54	1.54	1.54	0.29	0.06	34	
5B-1	7075 / Isoprep 177 / no desmut	1.75	2.88	2.88	3.13	3.13	3.13	1.38		0	Most of the area exposed during the initial crack failed adhesively. There were 100% adhesive failures beyond the crack tip (from breaking apart the wedges).
5B-2		1.88	3.30	3.30	3.38	3.38	3.38	1.50		0	
5B-3		2.00	3.35	3.35	3.50	3.50	3.50	1.50		0	
5B-4		1.54	2.76	2.76	2.90	2.90	2.90	1.36		0	
5B-5		1.48	2.23	2.49	2.71	2.71	2.71	1.23		0	
5B-avg		1.73	2.90	2.96	3.12	3.12	3.12	1.39	0.11	0	
6A-1	2024 / grit-blast	1.10	1.17	1.22	1.22	1.22	1.22	0.12		98	Adhesive failures were limited to areas less than 0.05 inch from the edges.
6A-2		1.12	1.12	1.12	1.25	1.25	1.25	0.13		98	
6A-3		1.12	1.12	1.12	1.23	1.23	1.23	0.11		99	
6A-4		1.14	1.14	1.14	1.24	1.24	1.24	0.10		99	
6A-5		1.15	1.15	1.24	1.29	1.29	1.29	0.14		99	
6A-avg		1.13	1.14	1.17	1.25	1.25	1.25	0.12	0.02	99	
6B-1	7075 / grit-blast	1.28	1.28	1.28	1.37	1.37	1.37	0.09		100	Adhesive failures were limited to areas less than 0.05 inch from the edges.
6B-2		1.21	1.21	1.27	1.32	1.32	1.32	0.11		100	
6B-3		1.23	1.23	1.23	1.33	1.33	1.33	0.10		99	
6B-4		1.18	1.28	1.28	1.28	1.28	1.28	0.10		99	
6B-5		1.21	1.30	1.30	1.35	1.35	1.35	0.14		99	
6B-avg		1.22	1.26	1.27	1.33	1.33	1.33	0.11	0.02	99	

"Adhesive" failures are defined at the metal to sol-gel or sol-gel to primer interface as observed by visual inspection. Without further characterization, it is not readily distinguishable where these failures lie.

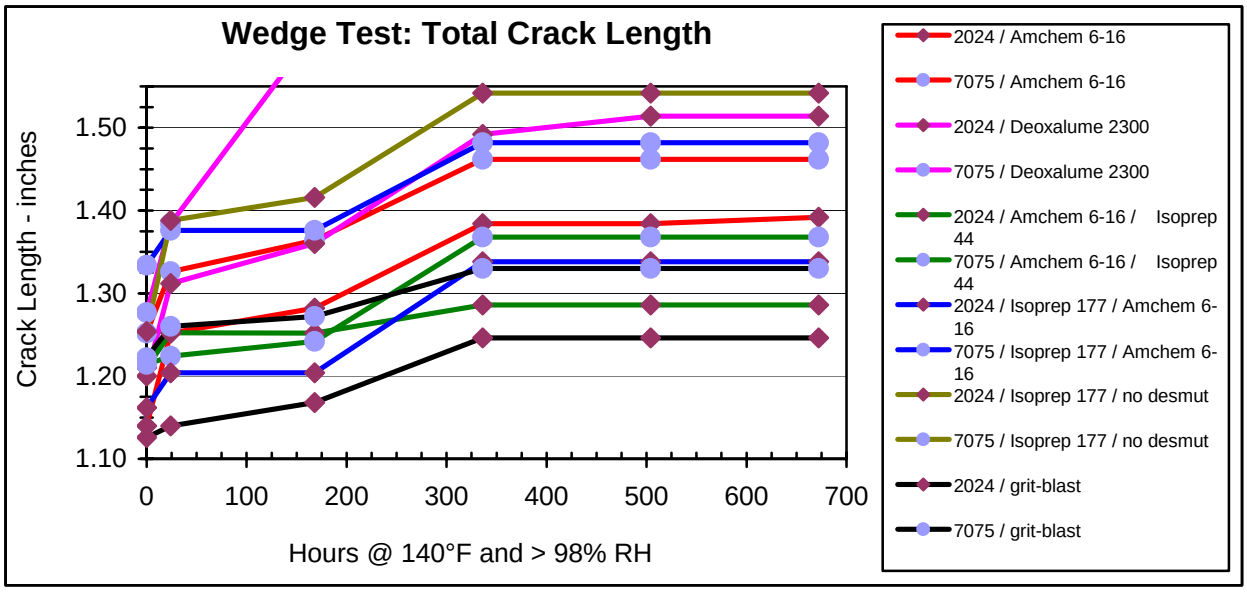


Figure 4.1-2 Wedge test data for aluminum chemical deoxidizers

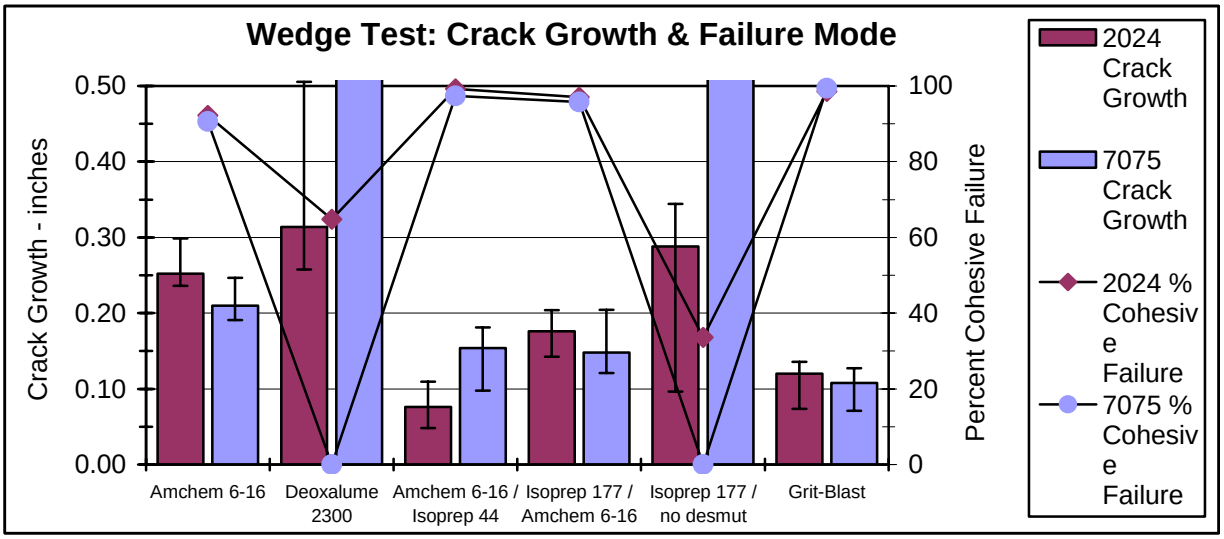


Figure 4.1-3 Wedge test growth and failure mode relationship for aluminum chemical deoxidizers

The wedge test proved to be a better discriminator than the peel test for this study. One set of specimens, deoxidation with Amchem 6-16 followed by immersion in the alkaline cleaning solution Isoprep 44, gave results that were comparable to the grit-blast controls. This sequence of processing was chosen so the final step in the chemical process was an alkaline solution, rather than an acidic deoxidizer. Wedge test crack growth was more extreme when Amchem 6-16 was the final step in the process (specimen 1).

Different deoxidizer chemistries yielded differences in the ultimate durability of the system. Deoxalume 2300 is an iron-based deoxidizer; Amchem 6-16 is a chromic acid based deoxidizer. Use of the acidic deoxidizer, Deoxalume 2300, led to greater amounts of crack growth and adhesive failure than use of Amchem 6-16. Use of Deoxalume was apparently alloy specific, as represented in the massive failure of 7075 alloy.

Alkaline etching followed by desmutting with Amchem 6-16 also gave good results with 2024 and 7075 alloys. Alkaline etching by itself (no desmut) resulted in a loss of environmental durability, as evidenced by the large crack growths and percentage of adhesive failures. This was possibly due to loosely adhered "smut" left on the aluminum alloy surface. The oxide-based smut layer did not leave a surface conducive to strong chemical bonding.

A mild alkaline conditioning after the deoxidation step was the best of the processes tested. Acid desmutting after an aggressive alkaline etching also gave good results. This may be due to the fact the aluminum substrate was immersed in the desmutting solution just long enough to remove the smut but not enough that the underlying surface was attacked by the acids.

4.1.2 Plasma Pretreatment of Aluminum Surfaces

Nontraditional methods of deoxidation were evaluated as means to eliminate additional hazardous materials from the bonding process. Plasma pretreatment was examined as an alternate method for cleaning, deoxidizing, and activating the metal surface prior to sol-gel application. Use of the plasma may reduce the need for cleaning solvents and the caustic or acidic etches associated with chemical deoxidation processes.

A "Flume" plasma system from PlasmaTreat-North America was used to clean and activate the surface of the aluminum alloy. This process blasts the surface of an object on the microscopic level using highly energized molecules and ions. The plasma head is in the open atmosphere and uses air as the plasma source. When using air as a plasma source, the oxygen reacts with contaminants on the surface of the object, producing a very clean surface, Figure 4.1-4. On organic surfaces, polar groups and active radicals are created that help increase surface adhesion by creating more chemically active functional groups over the surface which react with the subsequently applied adhesive coatings. In this study, the plasma source was rastered over the surface of the test specimen at a fixed rate and at different distances from the alloy surface. The specimen was subsequently treated with Boegel-EPII within 30 minutes of the cleaning treatment. The parts were primed and cured as previously described. Wedge test data and failure modes are shown in Table 4.1-4.

From these data, the failure modes indicate the closer the flume was to the surface, the less desirable the failure mode. Specimens activated at 0.25 in from the surface at 0.5 in/sec had 0% cohesive failure. Specimens activated at 0.5 in from the surface at a travel speed of 0.5 in/sec had the best failure modes with 95% cohesive failure. However, the baseline specimens, which were deoxidized in AmChem 6-16 with no plasma treatment, gave similar results. Thus, it is unclear from this study whether the plasma treatment provided any extra benefit on aluminum.

Figure 4.1-4 Plasma head used for pretreatment of metal alloys

Table 4.1-4 Plasma Pretreatment Wedge Test Data

Specimen No.	Plasma Parameter	Finger No.	Crack Length (inch) after Exposure to 140°F & > 98% RH (hrs)							Failure Location
			0	24	168	336	504	672	840	
1	1/4" @ 0.50 in/sec	1	1.08	1.08	1.53	1.62	1.67	1.67	1.67	0% cohesive
		2	1.11	1.11	1.54	1.60	1.67	1.67	1.67	0% cohesive
		3	1.13	1.13	1.35	1.40	1.45	1.45	1.45	0% cohesive
		4	1.22	1.22	1.50	1.56	1.56	1.60	1.60	0% cohesive
		5	1.24	1.24	1.64	1.70	1.73	1.73	1.73	0% cohesive
		average	**1.16**	**1.16**	**1.51**	**1.58**	**1.62**	**1.62**	**1.62**	**0% cohesive**
2	1/4" @ 1.00 in/sec	1	1.20	1.20	1.20	1.42	1.42	1.42	1.47	75% cohesive
		2	1.12	1.12	1.12	1.62	1.65	1.65	1.65	0% cohesive
		3	1.18	1.18	1.18	1.33	1.33	1.33	1.33	90% cohesive
		4	1.21	1.21	1.21	1.43	1.43	1.43	1.49	70% cohesive
		5	1.22	1.22	1.22	1.61	1.70	1.70	1.70	15% cohesive
		average	**1.19**	**1.19**	**1.19**	**1.48**	**1.51**	**1.51**	**1.53**	**50% cohesive**
3	1/2" @ 0.50 in/sec	1	1.32	1.32	1.48	1.48	1.48	1.48	1.48	95% cohesive
		2	1.18	1.18	1.34	1.34	1.34	1.34	1.34	95% cohesive
		3	1.28	1.28	1.28	1.40	1.40	1.40	1.40	95% cohesive
		4	1.21	1.21	1.41	1.41	1.41	1.41	1.41	95% cohesive
		5	1.28	1.28	1.44	1.44	1.44	1.44	1.44	95% cohesive
		average	**1.25**	**1.25**	**1.39**	**1.41**	**1.41**	**1.41**	**1.41**	**95% cohesive**
4	1/2" @ 1.00 in/sec	1	1.33	1.33	1.41	1.41	1.41	1.41	1.41	98% cohesive
		2	1.20	1.20	1.45	1.45	1.45	1.45	1.45	90% cohesive
		3	1.24	1.24	1.42	1.42	1.42	1.42	1.42	98% cohesive
		4	1.17	1.17	1.34	1.34	1.34	1.34	1.34	95% cohesive
		5	1.28	1.28	1.49	1.49	1.49	1.49	1.49	30% cohesive
		average	**1.24**	**1.24**	**1.42**	**1.42**	**1.42**	**1.42**	**1.42**	**82% cohesive**
5	none	1	1.23	1.23	1.23	1.42	1.42	1.42	1.42	95% cohesive
		2	1.23	1.23	1.23	1.39	1.39	1.39	1.39	95% cohesive
		3	1.17	1.17	1.17	1.32	1.32	1.32	1.40	98% cohesive
		4	1.27	1.27	1.27	1.48	1.48	1.48	1.48	80% cohesive
		5	1.22	1.22	1.22	1.41	1.41	1.41	1.41	95% cohesive
		average	**1.22**	**1.22**	**1.22**	**1.40**	**1.40**	**1.40**	**1.42**	**93% cohesive**

4.1.3 Titanium Manual Deoxidation Studies

A series of tests were conducted to optimize a nongrit-blast manual deoxidation procedure for adhesive bonding of titanium alloys. This type of process would be especially useful in repair and rework situations. In this test matrix, Ti-6Al-4V panels, 6 in x 6 in x 0.050 in were precleaned in an alkaline cleaner to remove loose soils and grease. Typically, solvent wiping would be employed in a repair setting to remove soil, but because of the number of specimens in this study, the panels were racked and cleaned in an immersion cleaner per Boeing specification BAC5749[11] to save time.

Two sets of wedge test panels were prepared per condition. Several types of abrasives and abrasive tools were used, based on similar abrasive work on aluminum alloys, to determine which methods would work best for the harder titanium alloys.

Panels were abraded using a two crosscoat abrasion pattern with a total abrasion time of approximately 1-2 minutes per specimen. Any excess titanium alloy or oxide residue was blown off with clean compressed air. Within 30 minutes of the abrasion process, panels were sprayed with Boegel-EPII solution for a period of two minutes. The panels were allowed to dry vertically and then were primed with Cytec BR 6747-1 primer. The primer was cured at 250°F, and the specimens were bonded with 3M AF 163-2OST adhesive. Panels were cut into 1 in strips and exposed at 140°F and >98% RH. The wedge test results are shown in Table 4.1-5 with panel wedge results reported as the average of 5 individual 1 in specimens.

Table 4.1-5 Wedge Test Results for Titanium Abrasion Study

Panel Set #	Abrasive	Abrasion Tool	Average Crack Length (inch) after Exposure to 140°F and >98% RH (hours)							Failure
			0	1	24	120	168	504	672	% coh
1A	Merit 120 grit A/O Resin Bond	ROS*	0.92	0.92	0.95	0.98	0.98	0.98	0.98	80
1B	Merit 120 grit A/O Resin Bond	ROS*	0.87	0.88	0.92	0.94	0.94	0.94	0.94	77
2A	Merit 180 grit A/O Resin Bond	ROS*	0.84	0.84	0.88	0.91	0.91	0.91	0.93	85
2B	Merit 180 grit A/O Resin Bond	ROS*	0.89	0.89	0.91	0.94	0.94	0.94	0.94	71
3A	Merit 240 grit A/O Resin Bond	ROS*	0.77	0.79	0.84	0.86	0.86	0.89	0.90	59
3B	Merit 240 grit A/O Resin Bond	ROS*	0.85	0.86	0.89	0.94	0.94	0.96	0.96	71
4A	3M Medium Scotch-Brite™	Right-Angle Die Grinder	0.80	0.80	0.85	0.88	0.88	0.92	0.92	48
4B	3M Medium Scotch-Brite™	Right-Angle Die Grinder	0.80	0.80	0.87	0.90	0.90	0.95	0.95	76
5A	Merit 120 grit Zirconia	Right-Angle Die Grinder	0.81	0.84	0.88	0.92	0.92	1.00	1.01	6
5B	Merit 120 grit Zirconia	Right-Angle Die Grinder	0.78	0.80	0.85	0.87	0.87	0.92	0.93	15
6A	Merit 120 grit A/O Resin Bond	Right-Angle Die Grinder	0.81	0.84	0.90	0.93	0.93	0.93	0.93	62
6B	Merit 120 grit A/O Resin Bond	Right-Angle Die Grinder	0.88	0.91	0.97	0.97	0.98	1.01	1.01	49
7A	Merit 180 grit A/O Resin Bond	Right-Angle Die Grinder	0.84	0.84	0.89	0.89	0.89	0.91	0.91	75
7B	Merit 180 grit A/O Resin Bond	Right-Angle Die Grinder	0.82	0.82	0.88	0.90	0.90	0.91	0.91	83

* Random Orbital Sander

Overall, there were areas of adhesive failure (at the metal interface) in all of the panels; more so than the comparable aluminum alloy coupons. Titanium alloys, in general, are much harder and more difficult to abrade to achieve a clean, uniform surface; this causes variability in testing and

performance. While the crack lengths tended to be fairly short overall, there were differences in the amount and type of adhesive failure.

It was difficult to observe trends in the data based on the abrasive used or the type of tool. The specimens of particular notice were those sanded with Merit 120 grit zirconia paper mounted on a die grinder. This particular combination tended to give fairly reproducible good results on aluminum alloys, but yielded the lowest cohesive failure rate in this study on titanium with an average of 10% cohesive failure. The grit size did not appear to be the cause of this effect since the Merit 120 grit alumina paper on the die grinder performed significantly better with approximately 56% cohesive failure. Using the adhesive-backed Merit 120 paper mounted on a random orbital sander, the failure mode was about 78% cohesive.

Within a panel set, there was a significant amount of variation between failure modes. For example, in Panel 3B, sanded with #240 grit alumina using a random orbital sander, the failure mode ranged from 5% cohesive on one specimen to 100% cohesive on the adjacent specimen. It is unclear what causes the differences in behavior. Grit size was also not a definitive indicator, as there was no clear trend in going from the largest to finest grit size in either the random orbital sanded or die grinder-sanded materials. The Scotch-Brite™-abraded materials were especially difficult to assess, with a wide degree of scatter within a given dataset.

In complementary testing, technicians at another site repeated a portion of this testing using the Merit #180 grit alumina resin bond media mounted on a random orbital sander. In these studies, the technicians had problems achieving a water-break-free surface after sanding. Review of their procedure identified several potential differences in procedure. Firstly, the specimens were solvent wiped with acetone prior to abrasion, whereas the specimens were alkaline cleaned in the first test. Secondly, the specimens were solvent wiped with acetone after abrasion in the complementary testing, whereas specimens were simply blown with dry compressed air in the original test. Solvent wipe testing has shown that water-breaks can occur on titanium alloys after solvent wiping with certain solvents. In general, the ketone-based solvents, such as methyl ethyl ketone or acetone, have been shown to cause changes in the surface wetting characteristics on titanium alloys. This might explain the issues that the technicians had in identifying a clean surface. It is preferred to clean the titanium surface with an alcohol based solvent, such as isopropanol, or clean water. Alternatively, abrasion debris can be removed using compressed clean air without solvent.

4.2 Abrasive Media Optimization Studies

4.2.1 Phase I Sandpaper Trials

Testing carried out to-date shows the process robustness that can be achieved when using the Merit #180 alumina grit “sandpaper: product. However, it would be useful to identify alternative abrasive papers, giving a second source for users to obtain appropriate supplies.

Previous testing[12] has shown the 3M sandpapers selected for this use gave variable results when used in conjunction with our sol-gel process. Thus, they were not selected for use with the sol-gel materials. In this Phase I testing, a trial was run to compare different abrasion media from various vendors. The results of the wedge test exposure data and failure modes for these trials are listed in Table 4.2-1. Panel data is reported as the average of 5 individual specimens.

Table 4.2-1 Wedge Test Data for Sandpaper Abrasion Trials

Panel No.	Surface Preparation	Initial Crack Length (in)	24-hour Crack Length (in)	1-week Crack Length (in)	4-week Crack Length (in)	Total Crack Growth (in)	%Coh
--	PAA	1.20	1.23	1.25	1.28	0.08	100
1	3M 210U-P180	1.14	1.30	1.37	1.39	0.25	98
2a	Merit SK-62-P180	1.18	1.30	1.30	1.34	0.16	98
3	Merit 120 Zirc Plus	1.18	1.31	1.31	1.32	0.14	98
4	3M 268L 80 Micron, 5" disc, Type D	1.18	1.31	1.40	1.42	0.24	98
5	3M 326U #220 alumina	1.21	1.36	1.48	1.51	0.30	85
7a	Scotch-Brite™ medium Roloc disc (maroon)	1.18	1.32	1.41	1.43	0.25	88

Climbing drum peel testing was also conducted at room temperature conditions. No distinct differences were seen in the dry peel strengths of the specimens with any of the abrasive media and techniques tested here, indicating there was not gross contamination of the surface using the abrasives and methods in this iteration. However, there were subtle differences in the wedge test performance of these specimens. Panel #5, abraded with the 3M 326U, yielded a greater crack growth and more adhesive failure than those abraded with the other sandpapers. This sandpaper was the original sandpaper tested from the historical testing, which was designed for use with non-metallic materials. The variability in the performance of the specimen abraded with the 3M 326U confirmed there is most likely some residue smeared on the surface using this abrasive paper, which accounts for the degradation in the hot/wet properties. The 3M abrasive papers gave slightly longer crack lengths than the Merit abrasive papers, but the failure modes after 4 weeks were fairly similar.

Additionally, the failure modes of the Scotch-Brite™ -abraded specimens, Panel #7a, were less acceptable in hot/wet wedge test testing than those for the majority of the sandpapers. Better results have been achieved in other testing using the Scotch-Brite™ materials[13]. Careful control of the abrasion methods used in conjunction with the Scotch-Brite™ may be required to prevent excessive deposition of contaminants on the surface due to smearing or overheating of the surface using the Scotch-Brite™ pads.

Double cantilever beam data were generated for several of these surface preparation methods and are shown in Figure 4.2-1. Four specimens were tested for each preparation. The environmental crack extension force (G_{1scc}) values reported are defined as the force required to propagate the crack under environmental exposure at 140°F and 95-100% relative humidity for 5 weeks. The results in Figure 4.2-1 show the sol gel specimens prepared with Merit 120 grit alumina performed equivalently to the anodized control samples. The specimens prepared with Merit 180 grit alumina and those prepared with the Type A Very Fine Scotch-Brite™ produced lower but acceptable force values. Increasing the media replacement from 3 times to 4 times paper replacement per panel slightly improved the values. Even with six paper changeouts, the 3M 268 product displayed problems with edge preparation. Finally, the 3M 210 abrasion did not result in acceptable performance for this test.

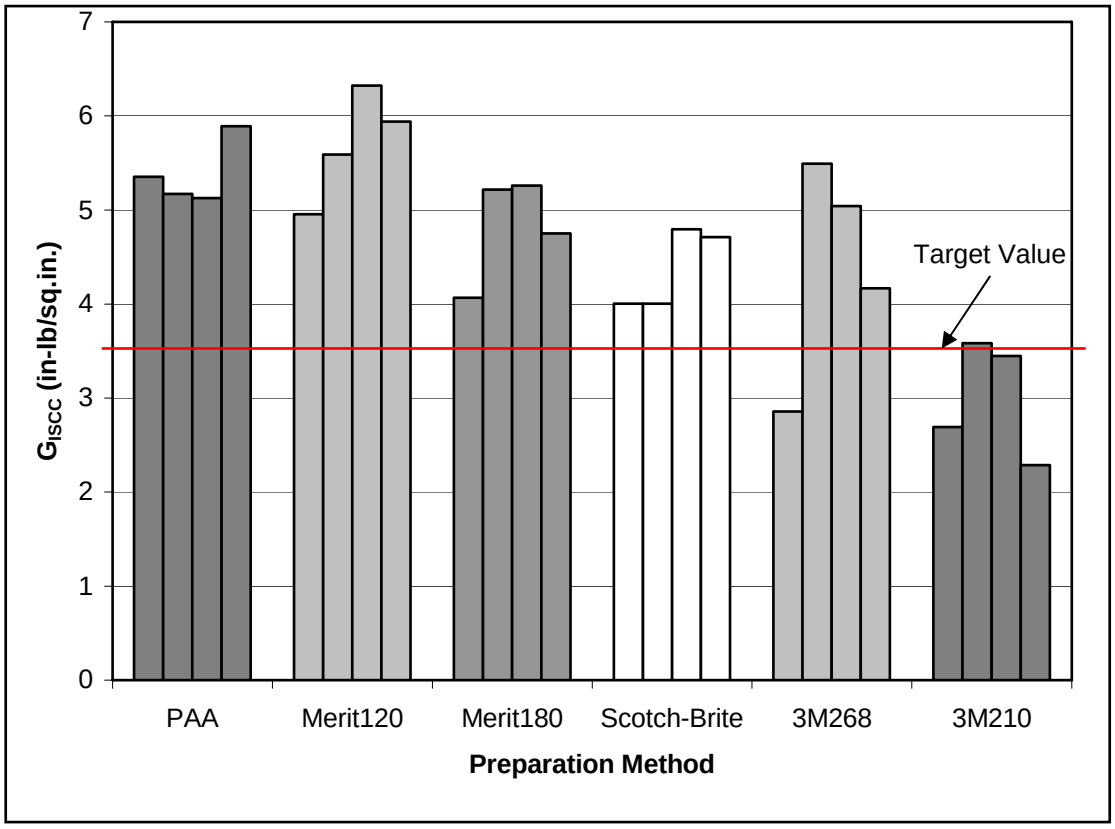


Figure 4.2-1 Double cantilever beam results for specimens prepared using different sandpapers.

As a result of these studies and accompanying surface analytical data, it was determined that the Merit papers gave the cleanest and most reproducible abraded surface. Subsequent to this, potential vendors were challenged to provide abrasive paper specimens that would reproducibly give good results with the sol-gel process procedures.

Phase II Sandpaper Testing:

Several new candidate abrasive papers were received from 3M. All were alumina-based grit and all were #180 grit size. The differences lay in the backing paper or cloth used to fabricate the sandpaper and the resin and loading system used to bond the grit to the abrasive pad surface. Three new 3M-brand sandpapers were tested for use as a pretreatment method prior to application of Boegel-EPII: 300D, 735U, and 900DZ.

There were some differences in the make-up of the sandpaper. For instance, the grit on the 300D was a naturally occurring alumina product, the 900 DZ had a man-made structured alumina, and the 735U was a mixture of both. The backing on the 300D and 900DZ was a J-weight cotton, whereas on the 735U, it was paper. The 735U has a third layer of coating on top of the alumina called a “no-fill” coating which is a non-stearate antistatic coating which is designed to prevent build up of sanding product from clogging the sandpaper.

Wedge test and peel specimens were fabricated using these abrasive paper candidates. Panels were abraded using a two crosscoat abrasion pattern with a total abrasion time of approximately 1-2 minutes per specimen. The data are shown in Table 4.2-2 and Figure 4.2-2. Climbing drum peel data is shown in Table 4.2-3.

Table 4.2-2 Wedge Test Data for 3M Abrasive Paper Trials

Specimen #	Crack Length (inch) after Exposure to 140°F & 98% RH (hours)								Total Crack Growth	StDev Crack Growth	% Cohesive Failure
	0	24	168	336	504	672	840	1008			
1-1	1.19			1.43	1.43	1.43	1.43	1.43	0.24		93
1-2	1.14			1.42	1.42	1.42	1.42	1.42	0.28		95
1-3	1.20			1.43	1.43	1.43	1.43	1.43	0.23		91
1-4*	1.42			1.64	1.64	1.64	1.64	1.64	0.22		67
1-5	1.14			1.43							93
3M 300 D	**1.24**			**1.48**	**1.48**	**1.48**	**1.48**	**1.48**	**0.24**	**0.0263**	**87**
2-1	1.30			1.65	1.70	1.70	1.75	1.75	0.45		0
2-2	1.28			1.55	1.55	1.55	1.55	1.55	0.27		33
2-3	1.14			1.50	1.50	1.50	1.50	1.50	0.36		33
2-4	1.20			1.47	1.47	1.47	1.47	1.47	0.27		33
2-5	1.17			1.50							25
3M 735 U	**1.23**			**1.54**	**1.56**	**1.56**	**1.57**	**1.57**	**0.34**	**0.0862**	**25**
3-1	1.18			1.41	1.41	1.41	1.41	1.41	0.23		93
3-2	1.16			1.38	1.44	1.44	1.44	1.44	0.28		93
3-3	1.27			1.49	1.49	1.49	1.49	1.49	0.22		80
3-4*	1.27			1.57	1.57	1.57	1.57	1.57	0.30		77
3-5	1.14			1.38							93
3M 900 DZ	**1.22**			**1.46**	**1.48**	**1.48**	**1.48**	**1.48**	**0.26**	**0.0386**	**86**
4-1	1.20			1.43	1.46	1.46	1.46	1.46	0.26		95
4-2	1.20			1.43	1.48	1.48	1.48	1.48	0.28		93
4-3*	1.25			1.45	1.45	1.45	1.45	1.45	0.20		73
4-4	1.14			1.38	1.42	1.42	1.42	1.42	0.28		93
4-5	1.19			1.45							93
Merit ARB	**1.20**			**1.42**	**1.45**	**1.45**	**1.45**	**1.45**	**0.26**	**0.0379**	**89**
There are no data for 24 and 168 hour exposure.											
Specimen 5 from each panel set was broken open at 2 weeks to observe failure mode.											
Values for specimen 5 are reported but are not included in charts or average values.											
* Specimens with poor cohesive failure results are from one end of the wedge test panel where the adhesive film appears to be thinner (1-4, 3-4 & 4-3).											

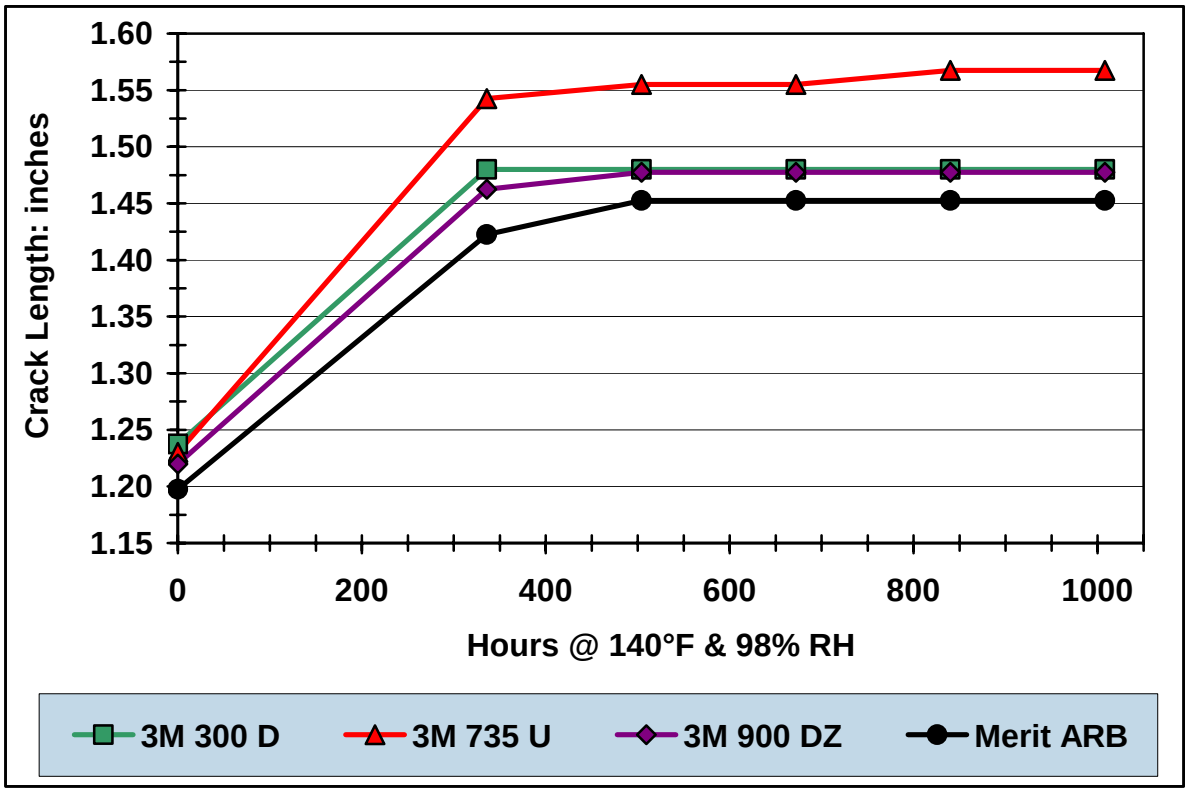


Figure 4.2-2 Wedge test growth for 3M sandpaper trials

Table 4.2-3 Climbing Drum Peel Data for 3M Abrasive Paper Candidates

	specimen 1		specimen 2		specimen 3		Average peel strength	
	lbf/in	% coh failure	lbf/in	% coh failure	lbf/in	% coh failure	lbf/in	St. Dev.
3M 300 D	87.9	100	88.9	100	92.8	100	89.9	2.6
3M 735 U	89.1	100	89.3	100	90.8	100	89.7	0.9
3M 900 DZ	88.1	100	84.7	100	98.6	100	90.5	7.2
Merit ARB	107.2	100	96.1	100	96.5	100	99.9	6.3

While the climbing drum peel data did not effectively differentiate between the abrasive papers used, there was a distinct difference in the failure modes observed in the wedge test specimens. The specimens abraded with the 735U paper performed significantly worse than the other papers. This is the candidate that had the non-stearated, no-fill coating.

4.3 Primer Studies

4.3.1 Temperature/Time Curing Optimization for BR 6747-1 Cure

This study was performed in conjunction with Naval Air System Command and was meant to simulate typical repair situations. The purpose was to determine the optimum time/temperature curve for curing BR 6747-1 bond primer when the recommended temperature of 250°F cannot be met due to limitations and constraints encountered during actual repairs.

The "solvent rub" test was used to get a rough idea of the acceptable time/temperature ranges to use in the study. Aluminum test panels were mechanically abraded using Merit 180 grit aluminum oxide discs on a right-angle die grinder. Boegel-EPII was brush applied and allowed to dry under ambient conditions. BR 6747-1 bond primer was brush applied using a foam brush. The primer was then cured according to the times and temperatures listed in Table 4.3-1. An oven was used to cure these test specimens instead of a heat blanket, because they are being used only for screening.

In the solvent rub test, methyl ethyl ketone (MEK) was applied to the test specimen and allowed to puddle on the surface for approximately 5 seconds. Rymple cloth was then used to rub the surface of the test specimen using a back and forth motion. Each specimen was rubbed using a total of 25 strokes. A rub in each direction was considered one stroke (i.e. back and forth = 2 strokes). A firm downward pressure was applied during the rub.

Evaluation of the rubbed surface was performed visually and with a Fischer Technology, Inc. Model MP2 Isoscope. The test results are presented in Table 4.3-1.

Table 4.3-1 Solvent Rub Test Results

Cure Temp (°F)	Cure Time (hrs)	Thickness (mil) before MEK			Thickness (mil) after MEK			% Coating Removed	Visual Observation
		1	2	3	1	2	3		
250	0.5	0.14	0.31	0.40	0.22	0.27	0.27	11	Pass
250	**1.0**	0.39	0.45	0.26	0.18	0.38	0.32	20	Pass
250	1.5	0.10	0.20	0.25	0.12	0.19	0.19	9	Pass
250	2.0	0.19	0.30	0.32	0.20	0.25	0.29	9	Pass
220	1.0	0.07	0.11	0.17	0.00	0.00	0.00	100	Fail
220	1.5	0.14	0.18	0.25	0.05	0.12	0.14	46	Marginal
220	**2.0**	0.03	0.09	0.16	0.06	0.08	0.09	18	Pass
200	1.0	0.16	0.14	0.11	0.00	0.00	0.00	100	Fail
200	1.5	0.15	0.23	0.25	0.00	0.00	0.00	100	Fail
200	2.0	0.12	0.16	0.22	0.00	0.05	0.00	90	Fail
200	**3.0**	0.12	0.24	0.23	0.08	0.11	0.13	46	Pass
180	4.0	0.15	0.27	0.18	0.00	0.02	0.00	97	Fail
180	6.0	0.12	0.25	0.28	0.07	0.13	0.13	49	Marginal
180	**8.0**	0.21	0.21	0.16	0.07	0.12	0.03	62	Marginal
150	4.0	0.07	0.10	0.07	0.00	0.00	0.00	100	Fail
150	6.0	0.20	0.12	0.09	0.00	0.00	0.00	100	Fail
150	8.0	0.27	0.22	0.17	0.00	0.00	0.00	100	Fail

Visual examination consisted of determining if the primer was removed during the test. It was typical to see primer on the Rymple cloth after each test. A test specimen was considered to have passed if little or no difference could be seen on the rubbed surface of the primed metal alloy. A marginal rating was assigned to test specimens that had visibly thinner primer remaining but still had primer left on the surface. Test specimens that showed bare spots were considered failures. The visual examination was made independently of the isoscope measurements.

Isoscope measurements were made to determine differences in the primer thickness before and after the solvent rub test. A mask with cutouts for the isoscope probe was used so that the same spots on each test specimen were measured before and after the rub test. The rough surface of the test specimen after mechanical abrasion contributed to the variation seen in the primer thicknesses. In some cases, the measured thickness of the primer was greater after rubbing and cast some doubt as to the usefulness of the thickness measurements.

A second series of tests were performed based on the curing of the primer as tested by the solvent rub test. The test matrix includes four time/temperature points (Specimens 2,3,4,5) that had been identified as acceptable primer cure conditions in a previous Air Force report.[14] The 250°F/1 hr, 220°F/2 hr and 200°F/3 hr combinations all produced passing results from the rub test. The 180°F/6 hr and 180°F/8 hr both produced marginal results. None of the 150°F cure specimens produced an acceptable result, but it was decided to try one with a 16 hour (overnight) cure. A control set is included. The controls were mechanically abraded but the primer was spray applied and oven-cured. The test matrix is presented in Table 4.3-2.

Table 4.3-2 Time/Temp Primer Cure Test Matrix

Specimen Number	**1**	**2**	**3**	**4**	**5**	**6**	**7** control	**8** control	**9**	**10**	**11** control
Cure Temperature (ºF)	250	220	200	180	180	150	250	250	210	200	250
Cure Time (hours)	1	2	3	6	8	16	1	1	3	4	1

Substrates for all tests were composed of 7075-T6 bare aluminum. The substrates were aqueous degreased and alkaline cleaned. A die grinder was used to abrade the aluminum surface using Merit #180 grit aluminum oxide disks. Within 30 minutes of abrasion, the Boegel-EPII was applied by hand using a foam brush.

Cytec BR 6747-1 primer was applied between 1 and 24 hours after sol-gel application. Specimens 1 – 6 and 9 – 10 were primed by hand using a foam brush and cured with a heat blanket. Specimens 7, 8 and 11 were the controls and were primed using an HVLP spray gun and oven cured. In this series, the primer was cured using a heat blanket All test specimens for each cure condition (except controls) were cured using the same heat blanket. The cures were conducted in a vacuum bag using house vacuum (approximately 23.5 in Hg).

Test specimens were assembled using EA 9394 paste adhesive. Scrim cloth (nylon 6-6, random mat, nonwoven filter media, 0.005 in, Hanna & Assoc.) was used for bondline thickness control. The bonded assemblies were cured in a vacuum bag under ambient (room temperature) conditions for 8 hours minimum. The bags were then vented to atmosphere and the assemblies

were allowed to cure for a minimum of 5 days. Figure 4.3-1 shows the bag assembly and temperature controller.

The test specimens for each of the cure conditions consisted of one set of climbing drum peel, one set of sustained stress lap shear, one set of lap shear, one set of wedge test and one specimen for the solvent rub test. The sustained stress lap shear were loaded to 1500 psi and exposed to 140°F and 98% relative humidity for 30 days. The wedge test specimens were exposed to 120°F and 98% relative humidity for 168 hours.

An optimized temperature profile was developed to provide a uniform temperature across the surface of all the test specimens that is within +/- 10°F of the temperature set point. Figure 4.3-2 and Figure 4.3-3 show examples of an early and optimized temperature profile.

Figure 4.3-1 Vacuum bag assembly and temperature controller

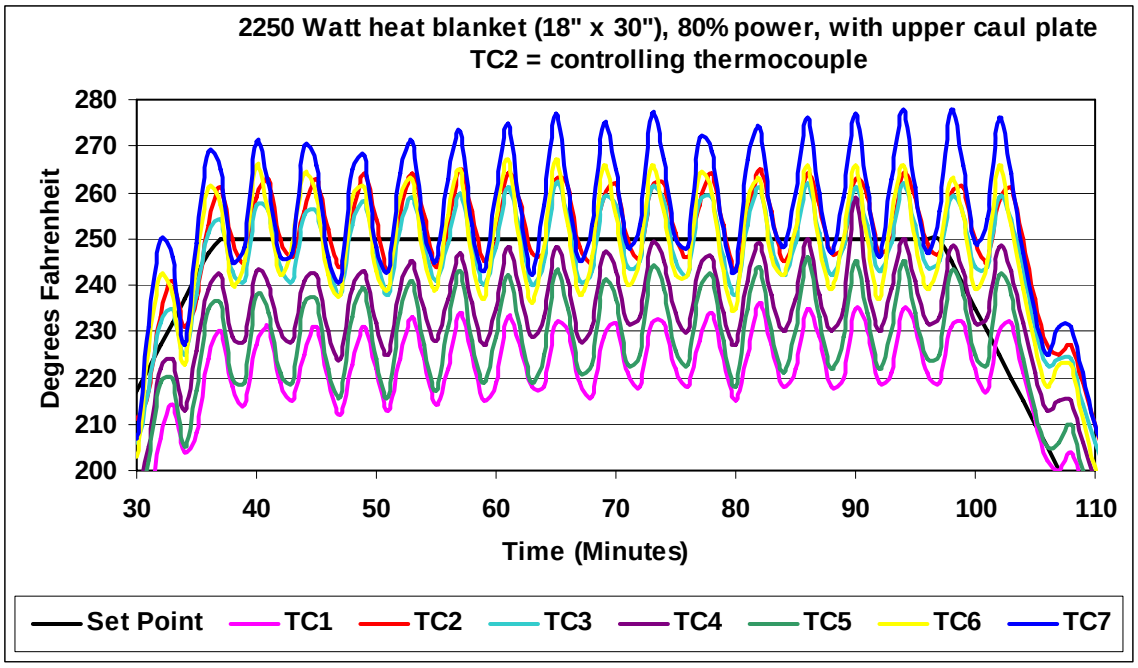


Figure 4.3-2 Early temperature profile for heat blanket primer curing

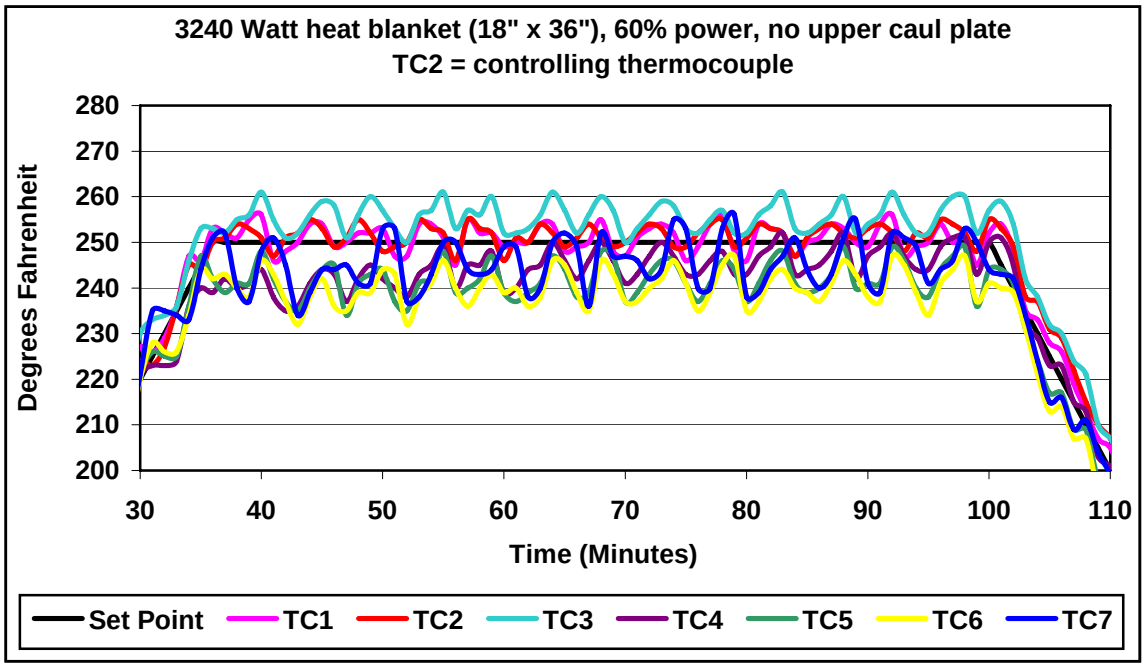


Figure 4.3-3 Optimized temperature profile for heat blanket primer curing

See Figure 4.3-4 and Figure 4.3-5 for bag, layup and cure configuration.

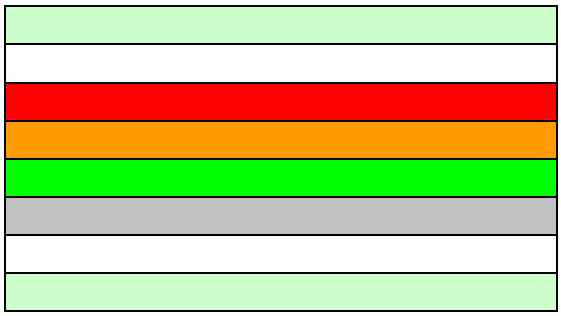
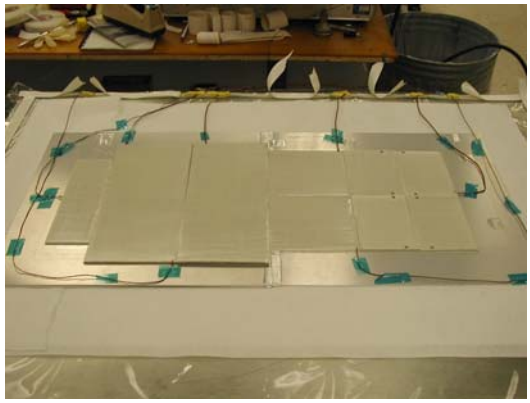
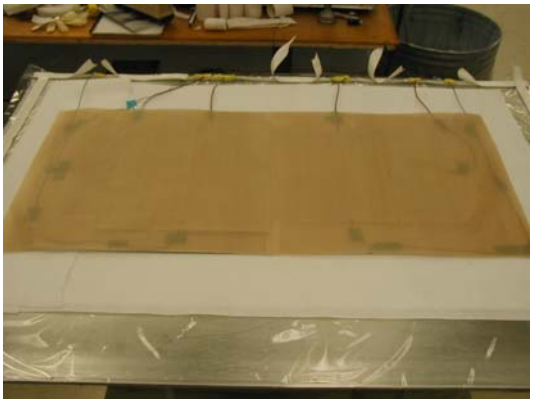


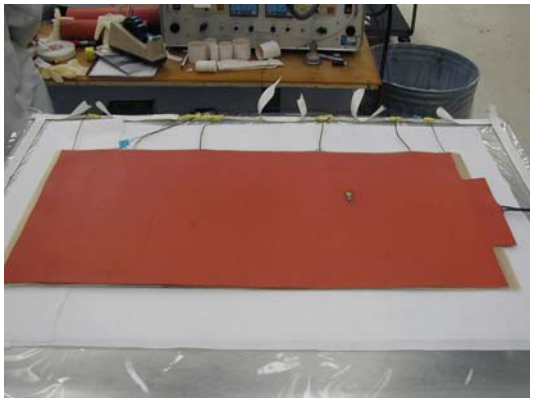
Figure 4.3-4 Vacuum bag configuration



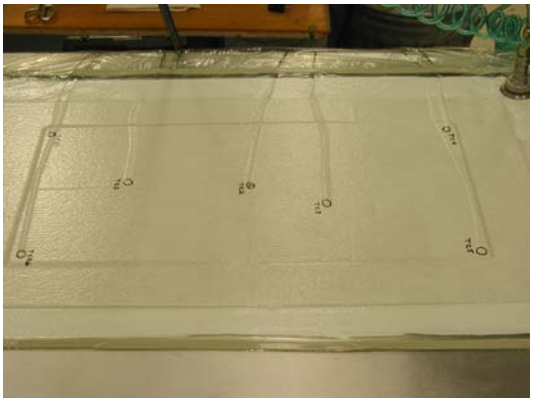
a.) Primed Test Specimens



b.) Application of Teflon Release Film



c.) Application of Heat Blanket



d.) Completed Bag

Figure 4.3-5 Layup for primer cure

Test results are presented below in Table 4.3-3 Table 4.3-4, Table 4.3-5, Figure 4.3-6, Figure 4.3-7, and Figure 4.3-8. Panel results are listed as an average of five individual specimens

Table 4.3-3 Peel Strength Test Results for Time/Temp Primer Cure Study

Panel No.	Cure Temp (°F)	Cure Time (hours)	Avg lbf/inch		Avg % cohesive failure		Notes on failure modes
			Mean	StDev	Mean	StDev	
1	250	1	20	1	96	3	Cohesive failure = failure within the adhesive. All noncohesive failure was within the BR 6747-1 primer. Specimens No. 9, 10 and 11 showed evidence of insufficient adhesive. Comb marks through the adhesive were exposing traces of the primed surface. The most likely cause was insufficient adhesive to properly flow after pressure was applied. Although primer was visible, the cause was not adhesive failure at the primer-adhesive interface.
2	220	2	15	3	60	27	
3	200	3	11	2	83	30	
4	180	6	4	1	1	2	
5	180	8	7	2	14	6	
6	150	16	0	0	0	0	
7	250	1	12	1	92	8	
8	250	1	15	0	100	0	
9	210	3	18	1	100	0	
10	200	4	19	1	100	0	
11	250	1	15	1	100	0	

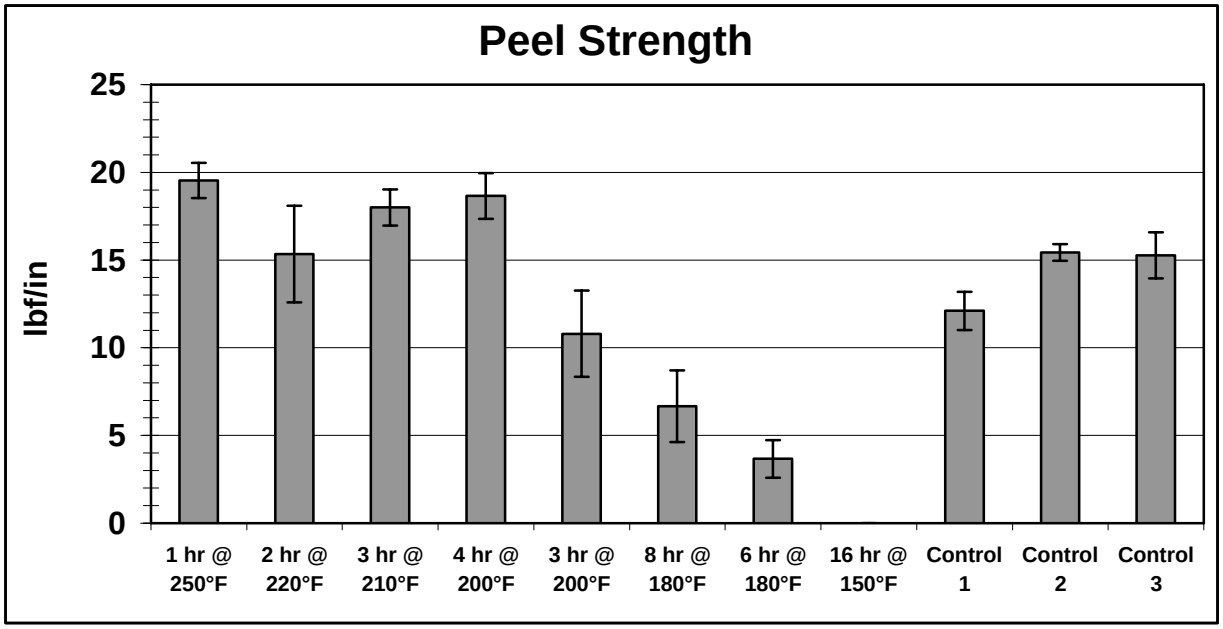


Figure 4.3-6 Peel strength test results for time/temp primer cure study

Table 4.3-4 Room Temperature Lap Shear Strength Test Results for Time/Temp Primer Cure Study

Panel No.	Cure Temp (°F)	Cure Time (hours)	Avg psi		Avg % cohesive failure	
			Mean	StDev	Mean	StDev
1	250	1	3550	114	87	4
2	220	2	3459	196	87	4
3	200	3	3185	357	84	7
4	180	6	3180	366	42	16
5	180	8	3161	209	86	9
6	150	16	1158	104	0	0
7	250	1	2738	211	97	1
8	250	1	3222	125	90	3
9	210	3	3229	50	99	1
10	200	4	2785	262	100	1
11	250	1	2973	33	100	1

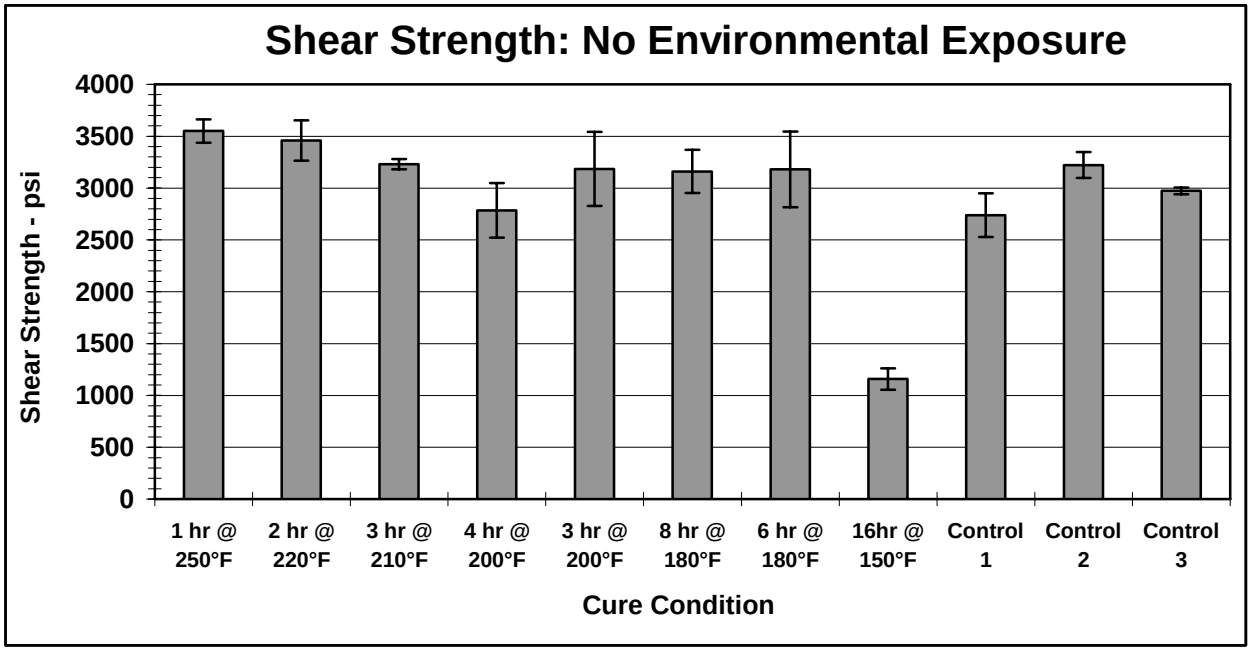


Figure 4.3-7 Lap shear strength test results for time/temp primer cure study

The sustained stress lap shear panels were loaded into the temperature and humidity cabinet for a 30 day exposure. All specimens were discovered to have failed sometime during the first 18 days. This included the control set. This was unexpected, because in previous tests there were no failures in the 30 day period. The cause for these failures is unknown. Visible observation of the failure modes shows the failures to be predominantly cohesive within the EA 9394 paste epoxy adhesive.

Table 4.3-5 Wedge Test Results for Time/Temp Primer Cure Study

Panel. No.	Temp	Time	Crack Length after Exposure to 120°F & > 98% RH (hours)						Total Crack Growth	Std. Dev.	% Coh. Failure
			0	1	24	48	120	168			
1	250	1	1.98	2.47	2.49	2.53		2.53	0.55	0.04	100
2	220	2	1.95	2.39	2.39	2.42		2.42	0.47	0.12	100
3	200	3	1.98	2.41	2.42	2.46		2.46	0.48	0.05	100
4	180	6	1.85				2.44	2.44	0.59	0.14	66
5	180	8	2.07				2.61	2.61	0.54	0.08	100
6	150	16	3.68								0
7	250	1	2.08	2.47	2.47	2.55		2.55	0.47	0.13	100
8	250	1	1.96				2.55	2.55	0.59	0.07	100
9	210	3	1.97	2.54	2.54	2.54		2.54	0.58	0.11	
10	200	4	1.88	2.18	2.18	2.18		2.18	0.29	0.29	
11	250	1	1.95	2.46	2.46	2.46		2.46	0.51	0.16	

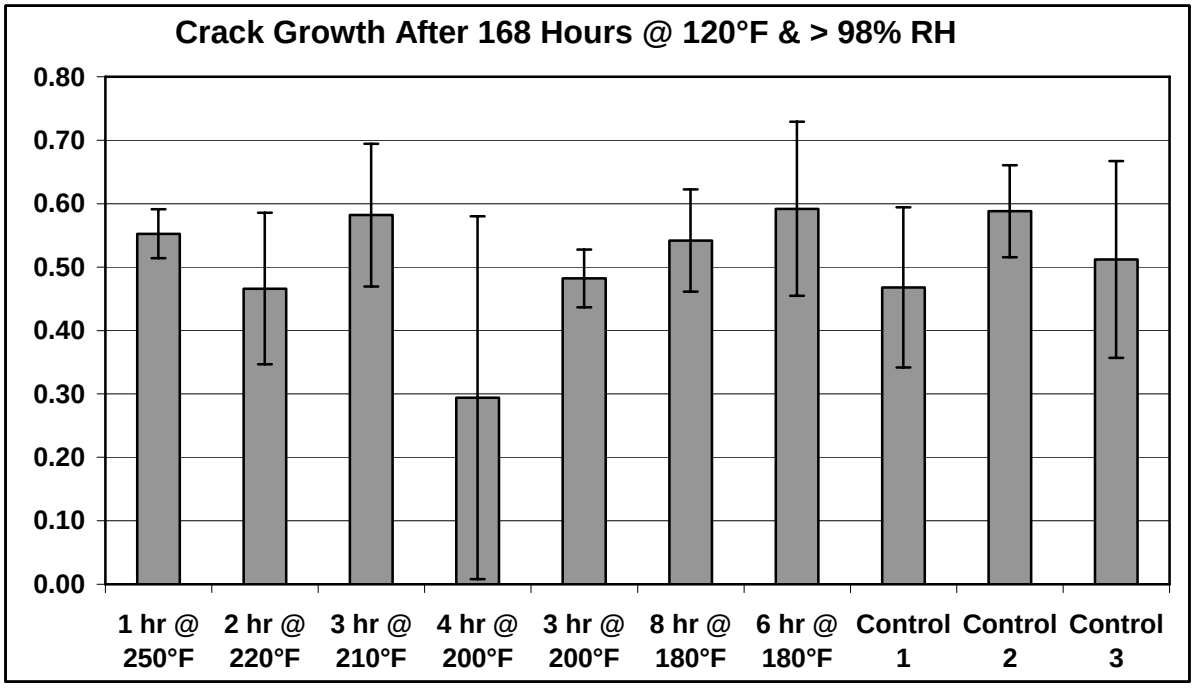


Figure 4.3-8 Wedge test crack growth for time/temp primer cure study

Panels #9, 10 and 11 (colored columns) had evidence of insufficient adhesive. Comb marks through the adhesive were exposing traces of the primed surface. The most likely cause was insufficient adhesive to properly flow after pressure was applied.

Table 4.3-6 MEK Rub Test for Primer Cure Time/Temp Study

ID	Cure Temp (F)	Cure Time (hrs)	Thickness (mil) before MEK			*Thickness (mil) after MEK*			% Coating Removal	Visual Observation	Comments
			1	2	3	1	2	3			
1	250	1.0	0.17	0.19	0.21	0.17	0.20	0.21	-2	Pass	
2	220	2.0	0.22	0.17	0.19	0.14	0.22	0.21	2	Pass	
3	200	3.0	0.25	0.23	0.20	0.28	0.15	0.15	15	Pass	
4	180	6.0	0.29	0.30	0.28	-0.01	-0.01	0.08	93	Fail	blotches of bare areas
5	180	8.0	0.28	0.23	0.24	0.15	0.18	0.14	37	Pass	
6	150	16.0	0.65	0.75	0.64	0.02	-0.02	0.04	98	Fail	wiped bare on first stroke
7	250	1.0	0.14	0.10	0.18	0.18	0.15	0.15	-14	Pass	
8	250	1.0	1.19	1.18	1.19	1.27	1.43	1.33	-13	Pass	applied too thick
9	210	3	0.13	0.15	0.15	0.11	0.10	0.10	28	Pass	
10	200	4	0.16	0.19	0.15	0.10	0.11	0.11	36	Pass	
11	250	1	0.15	0.19	0.12	0.11	0.16	0.09	22	Pass	

The data above show the primer can be cured under a vacuum bag configuration using a variety of conditions. If the primer is not fully cured, the performance values start to drop off. This was demonstrated most easily in the climbing drum peel values. The lap shear and wedge test data were more variable, and the trends were not as clear as the climbing drum peel data.

These tests showed the primer can be fully cured at temperatures as low as 200°F. A minimum of 4 hrs would be required to achieve acceptable properties at this temperature condition. A drop-off in properties was seen when the primer was cured at 180°F. Incomplete cure was observed when heated to 150°F, even for long periods of time. Higher cure temperatures (>200°F) will likely give more robust curing results in a repair scenario, as the part temperature may be variable due to heat sinks and heat blanket configurations.

4.3.2 Boegel EPII / BR 6747-1 Primer Cocure / Precure Testing

The purpose of this test was to determine the effects of cocuring versus precuring of the adhesive bond primer with the adhesive in the bonded system. The effects of different adhesive chemistries with the uncured bond primer were the focus of this study. Three adhesives were used with the Boegel EPII / BR 6747-1 sol-gel conversion coating / primer system. Two pretreatment methods were utilized on the adherends prior to sol-gel application. The adherends were abraded with either a random orbital sander (ROS) using 180-grit Merit sandpaper or a right-angle die grinder (DG) using medium Scotch-Brite™. Table 4.3-7 lists the test matrix.

Table 4.3-7 Boegel-EPII / BR 6747-1 Cocure – Precure Test Matrix

Panel #	Abrasion Method	Primer Cure Method	Adhesive	Adhesive Specs
1	Scotch-Brite™	cocure	EA 9696	Loctite EA 9696 Grade 10, 0.06 lb/ft^2: Lot No. 3052, DOM* February 21, 2003
2	Merit 180			
3	Scotch-Brite™	cocure	FM 300	Cytec FM 300, 5 mil: Batch No. 04979, roll 0078, DOM December 01, 2003
4	Merit 180			
5	Scotch-Brite™	cocure	FM 73	Cytec FM 73 Grade 10, 0.06 lb/ft^2: Batch No. 01710, roll 0047, DOM February 15, 2003
6	Merit 180			
7	Scotch-Brite™	precure	EA 9696	Loctite EA 9696 Grade 10, 0.06 lb/ft^2: Lot No. 3052, DOM February 21, 2003
8	Merit 180			
9	Scotch-Brite™	precure	FM 300	Cytec FM 300, 5 mil: Batch No. 04979, roll 0078, DOM December 01, 2003
10	Merit 180			
11	Scotch-Brite™	precure	FM 73	Cytec FM 73 Grade 10, 0.06 lb/ft^2: Batch No. 01710, roll 0047, DOM February 15, 2003
12	Merit 180			

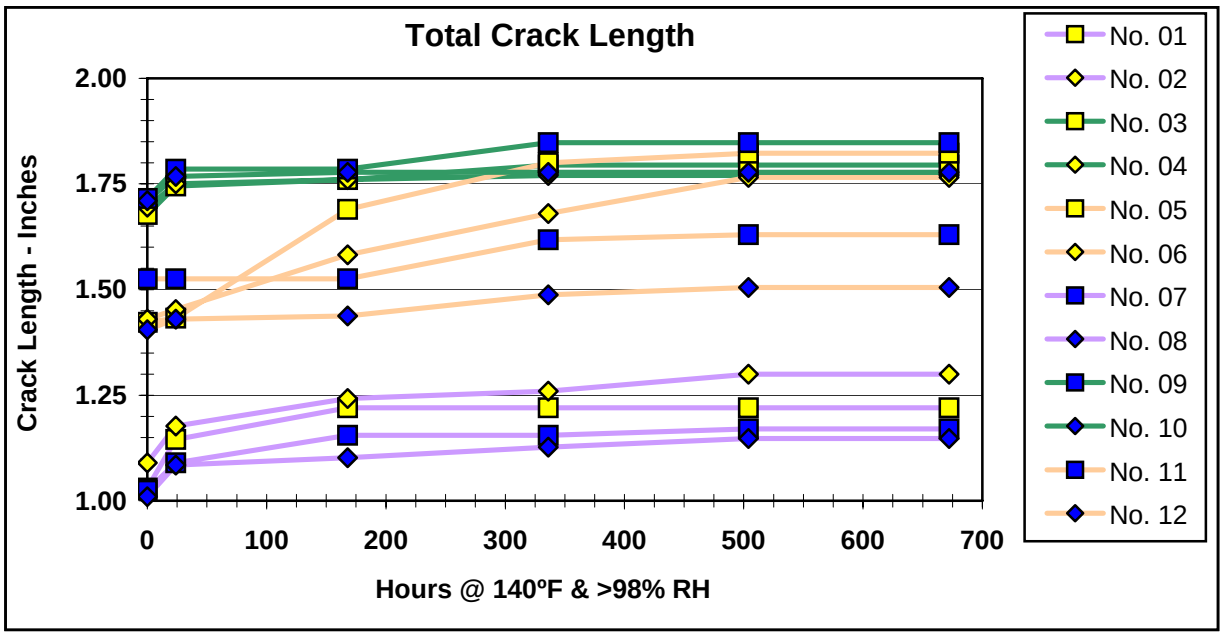
*DOM = Date of Manufacture

For this study, wedge test and lap shear test assemblies were prepared per ASTM D 3762 and BSS7202[15] Type IV, respectively, for each panel in the test matrix. Aluminum 2024-T3 bare alloy was used for all tests. Specimens were precleaned using Brulin 815GD and Isoprep 44 per BAC5763[16] and BAC5749 respectively. Specimens were then abraded as described in the test matrix for one minute per each 40 in^2. The abrasive material was changed every 30 seconds, and the direction of abrasion was changed by 90° after each abrasive material change.

Boegel-EPII was applied by HVLP, and the specimens were air dried for 30 minutes. A film of BR 6747-1 adhesive bond primer approximately 0.0002 in thick was applied by HVLP and air dried for 30 minutes. Cocure panel adherends were assembled into test assemblies 30 minutes after primer application. The primer was cured on the adherends for precured specimens for 75 minutes at 250°F. All substrates were arranged into test assemblies and cured per the applicable adhesive specifications. Cured assemblies were machined into individual test specimens per ASTM D 3762 and BSS7202 Type IV. Wedge test specimens were exposed to 140°F and >98% RH for 4 weeks. The results are shown in Table 4.3-8 and Figure 4.3-9 and Figure 4.3-10.

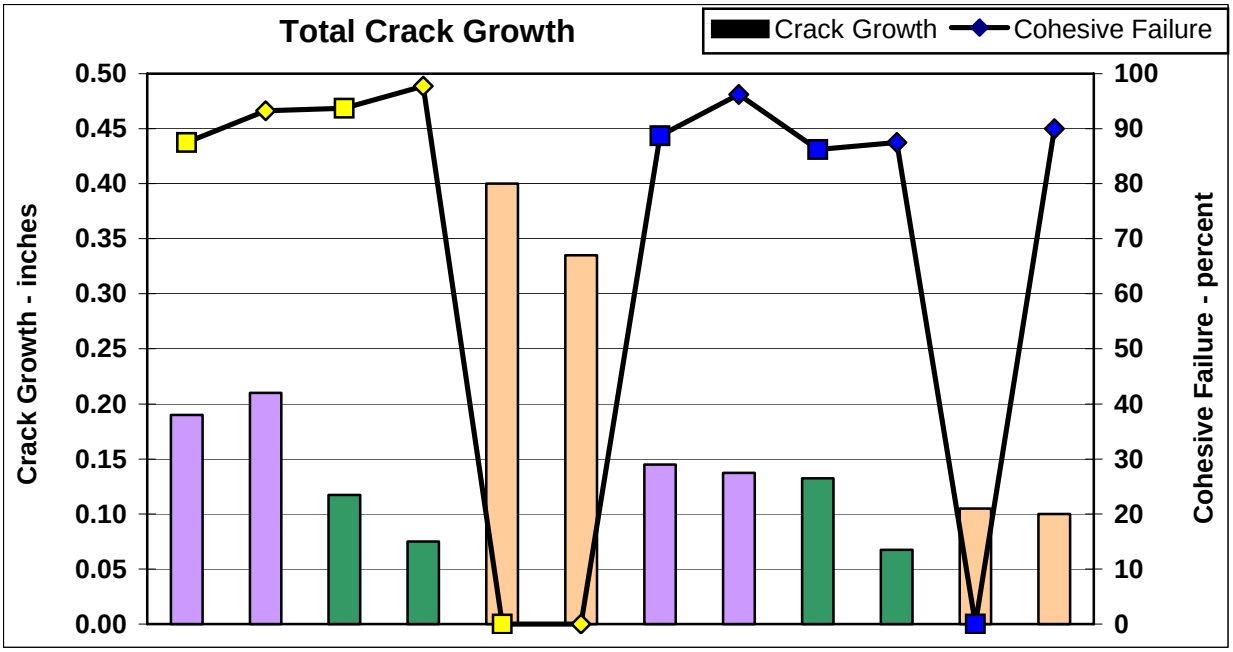
Table 4.3-8 Wedge Test Results for Primer Cocure Study

Panel No.	Abrasion Method	Adhesive	Cure Method	Crack Length (inch) after Exposure to 140ºF & >98% RH (hours)						Crack growth (inches)	% Coh. Failure
				0	24	168	336	504	672		
1	Scotch-Brite™	EA 9696	cocure	1.03	1.15	1.22	1.22	1.22	1.22	0.19	88
2	Merit 180	EA 9696	cocure	1.09	1.18	1.24	1.26	1.30	1.30	0.21	93
3	Scotch-Brite™	FM 300	cocure	1.68	1.75	1.76	1.80	1.80	1.80	0.12	94
4	Merit 180	FM 300	cocure	1.70	1.75	1.76	1.77	1.77	1.77	0.07	98
5	Scotch-Brite™	FM 73	cocure	1.42	1.43	1.69	1.80	1.82	1.82	0.40	0
6	Merit 180	FM 73	cocure	1.43	1.45	1.58	1.68	1.77	1.77	0.34	0
7	Scotch-Brite™	EA 9696	precure	1.03	1.09	1.16	1.16	1.17	1.17	0.15	89
8	Merit 180	EA 9696	precure	1.01	1.09	1.10	1.13	1.15	1.15	0.14	96
9	Scotch-Brite™	FM 300	precure	1.72	1.79	1.79	1.85	1.85	1.85	0.13	86
10	Merit 180	FM 300	precure	1.71	1.77	1.78	1.78	1.78	1.78	0.07	88
11	Scotch-Brite™	FM 73	precure	1.53	1.53	1.53	1.62	1.63	1.63	0.11	0
12	Merit 180	FM 73	precure	1.41	1.43	1.44	1.49	1.51	1.51	0.10	90



KEY	Yellow Square = Scotch-Brite™ Cocure
Violet Line = EA 9696	Yellow Diamond = Merit 180 Cocure
Green Line = FM 300	Blue Square = Scotch-Brite™ Precure
Orange Line = FM 73	Blue Diamond = Merit 180 Precure

Figure 4.3-9 Wedge test crack length for primer cocure study



KEY	Yellow Square = Scotch-Brite™ Cocure
Violet Column = EA 9696	Yellow Diamond = Merit 180 Cocure
Green Column = FM 300	Blue Square = Scotch-Brite™ Precure
Orange Column = FM 73	Blue Diamond = Merit 180 Precure

Figure 4.3-10 Total wedge crack growth for primer cocure study

A careful analysis of the failure modes on these specimens was conducted to gain a better understanding of the mechanism of failure and the relationship to the particular adhesive chemistry that was used. Photographs of the cocured-primer wedge test specimens are shown in Figure 4.3-11, and photos of the precured-primer wedge test specimens are shown in Figure 4.3-12.

The largest performance difference in wedge test performance between the precured and cocured primer occurred with the FM 73 adhesive. The initial crack lengths were all approximately the same, but the precured FM 73 specimens grew about 0.10 in over 4 weeks while the cocured FM 73 specimens grew 0.40 and 0.34 in for the Scotch-Brite™ and Merit 180 grit cases respectively, over the same period. The FM 73 specimens also exhibited the worst failure modes of the three adhesives. Both of the cocured and the Scotch-Brite™ precured specimens all had 100% adhesive failure at the metal to primer interface while the precured Merit 180 had only 10% adhesive failure.

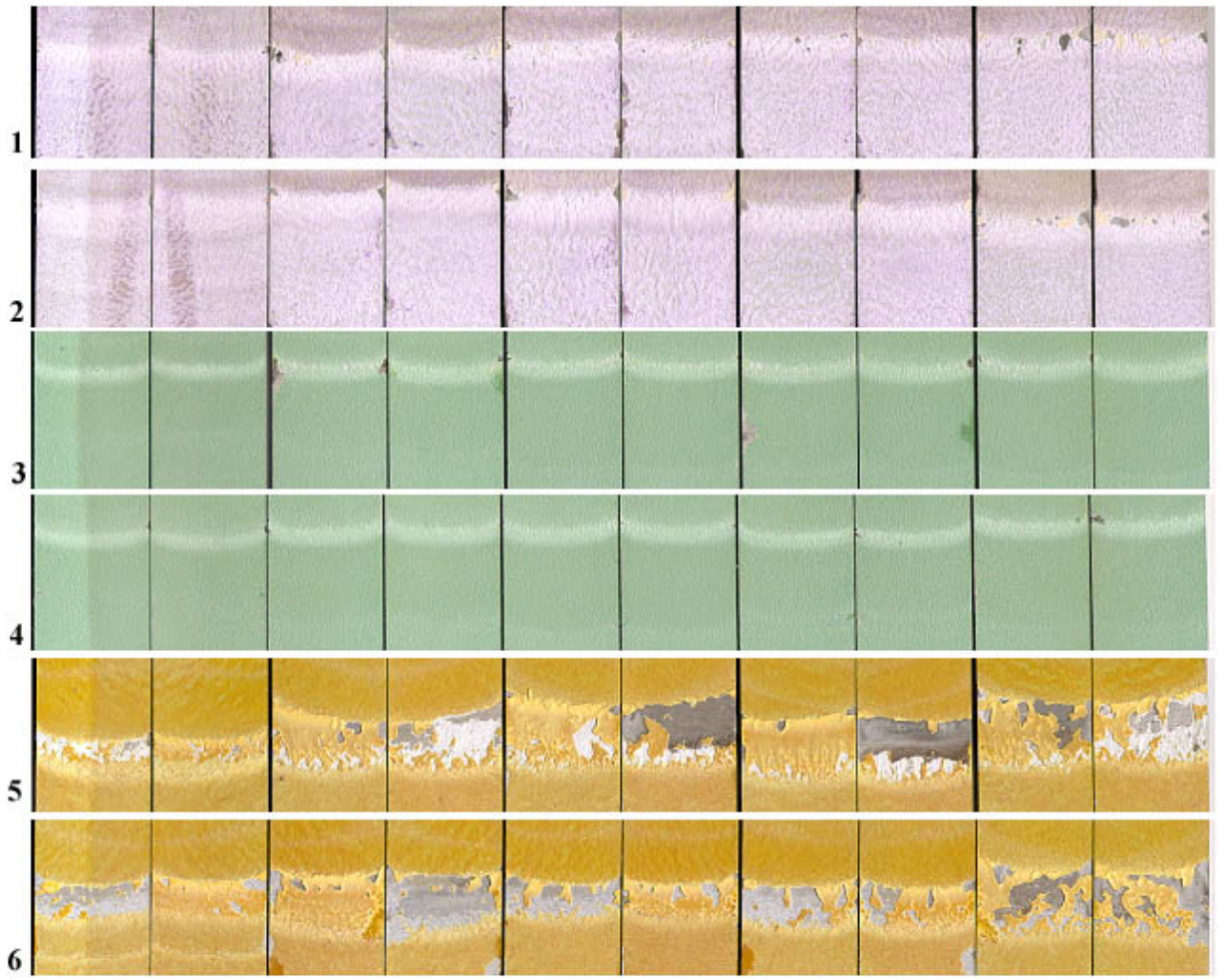


Figure 4.3-11 Cocured primer study wedge test specimen failure modes

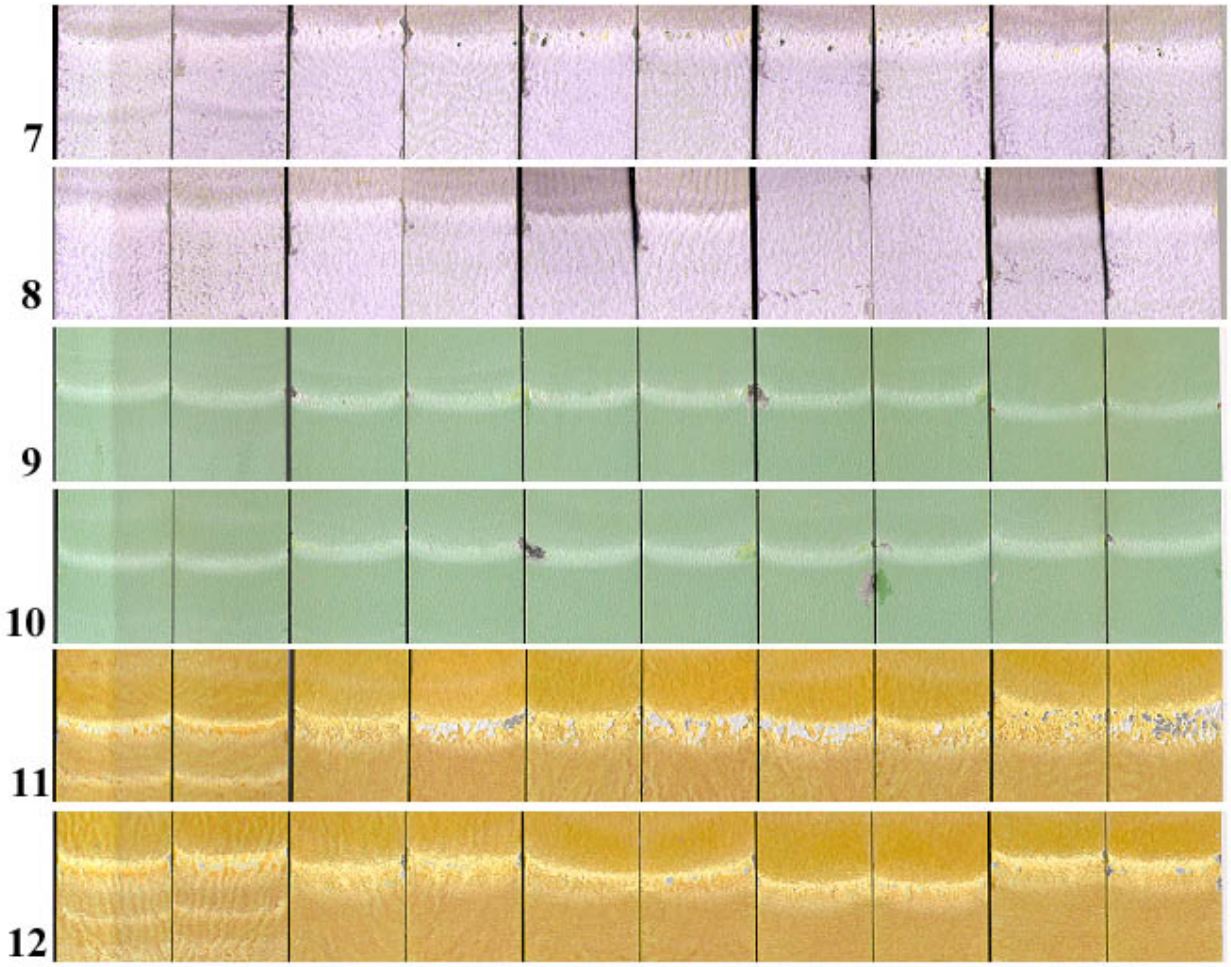
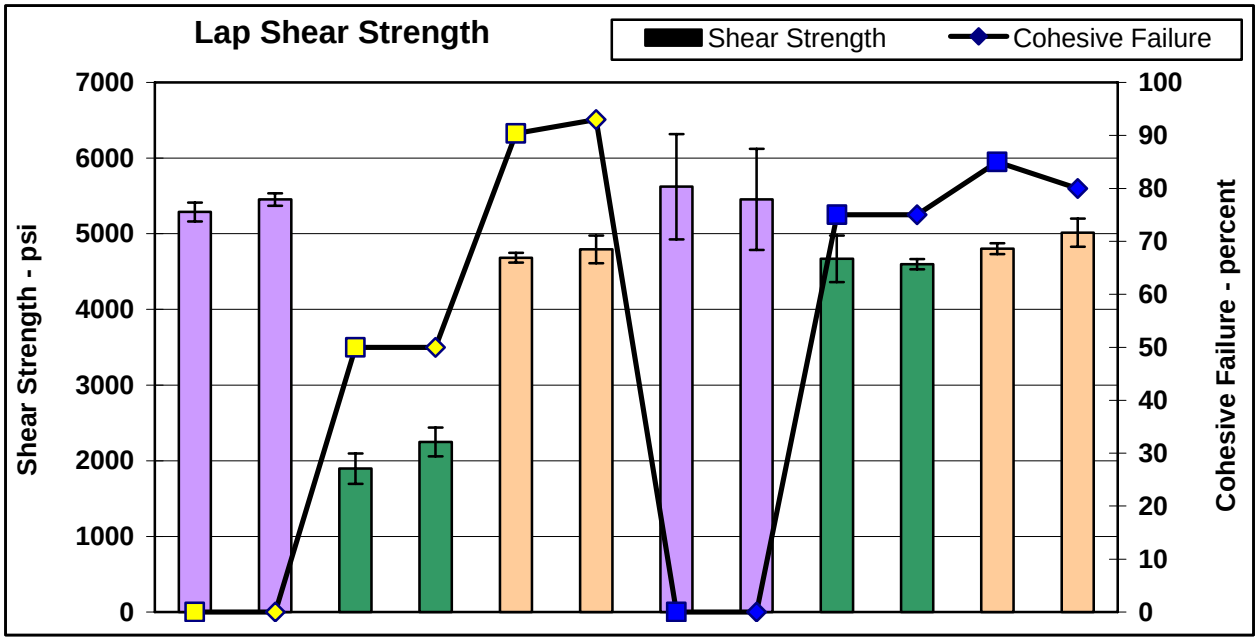


Figure 4.3-12 Precured primer study wedge test specimen failure modes

Room temperature lap shear test results for the cocure matrix are shown in Table 4.3-9 and Figure 4.3-13. Failure modes for the lap shear specimens are shown in Figure 4.3-14.

Table 4.3-9 Room Temperature Lap Shear Test Results for Primer Cocure Matrix

Panel No.	Abrasion Method	Adhesive	Cure Method	Shear Strength	St. Dev.	Cohesive Failure %
1	Scotch-Brite™	EA 9696	cocure	5289	125	0
2	Merit 180	EA 9696	cocure	5452	82	0
3	Scotch-Brite™	FM 300	cocure	1896	201	50
4	Merit 180	FM 300	cocure	2249	191	50
5	Scotch-Brite™	FM 73	cocure	4685	64	90
6	Merit 180	FM 73	cocure	4794	183	93
7	Scotch-Brite™	EA 9696	precure	5622	695	0
8	Merit 180	EA 9696	precure	5454	670	0
9	Scotch-Brite™	FM 300	precure	4669	308	75
10	Merit 180	FM 300	precure	4599	69	75
11	Scotch-Brite™	FM 73	precure	4800	72	85
12	Merit 180	FM 73	precure	5016	187	80



KEY	Yellow Square = Scotch-Brite™ Cocure
Violet Column = EA 9696	Yellow Diamond = Merit 180 Cocure
Green Column = FM 300	Blue Square = Scotch-Brite™ Precure
Orange Column = FM 73	Blue Diamond = Merit 180 Precure

Figure 4.3-13 Shear strength and failure mode for primer cocure matrix

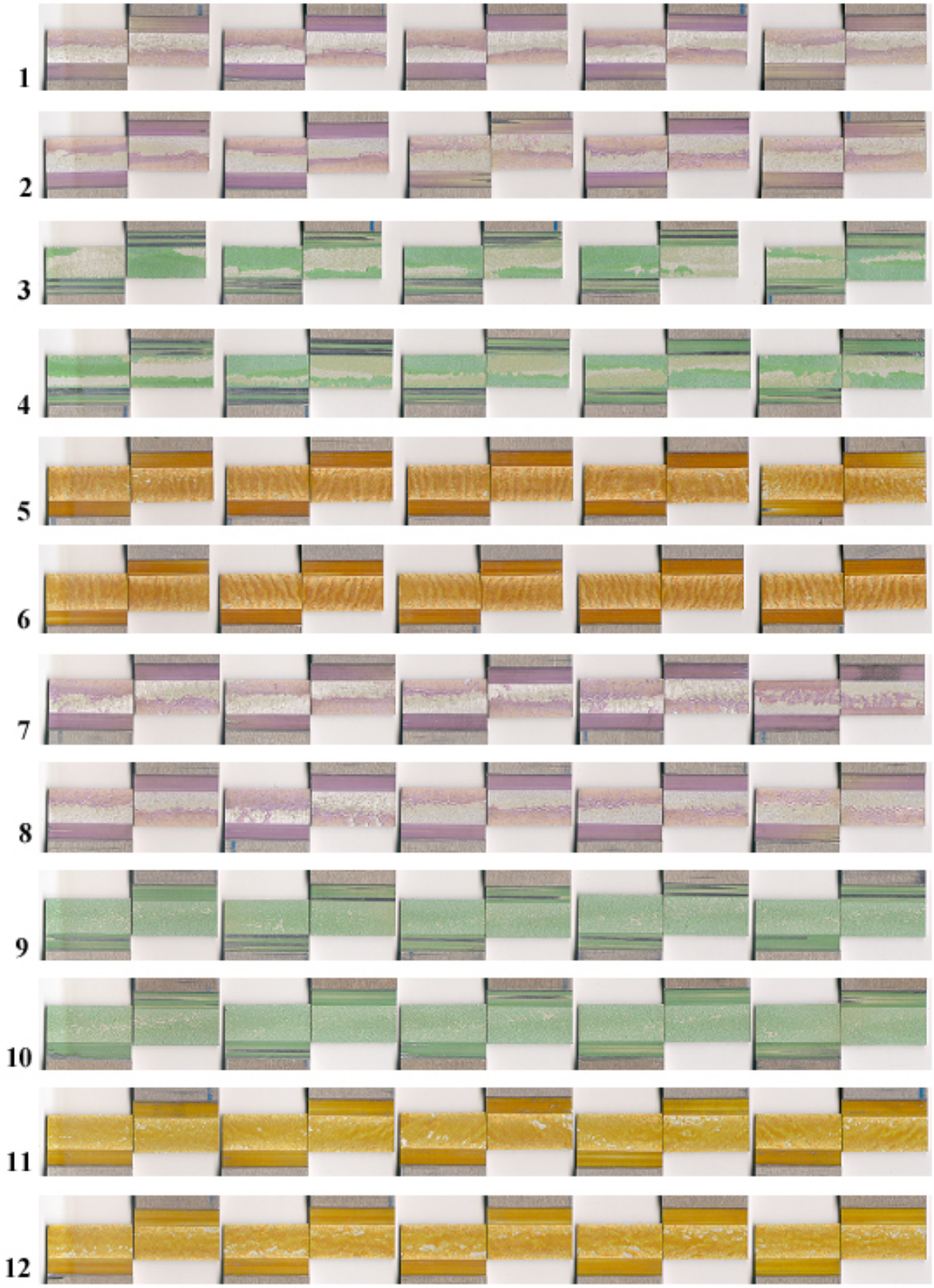
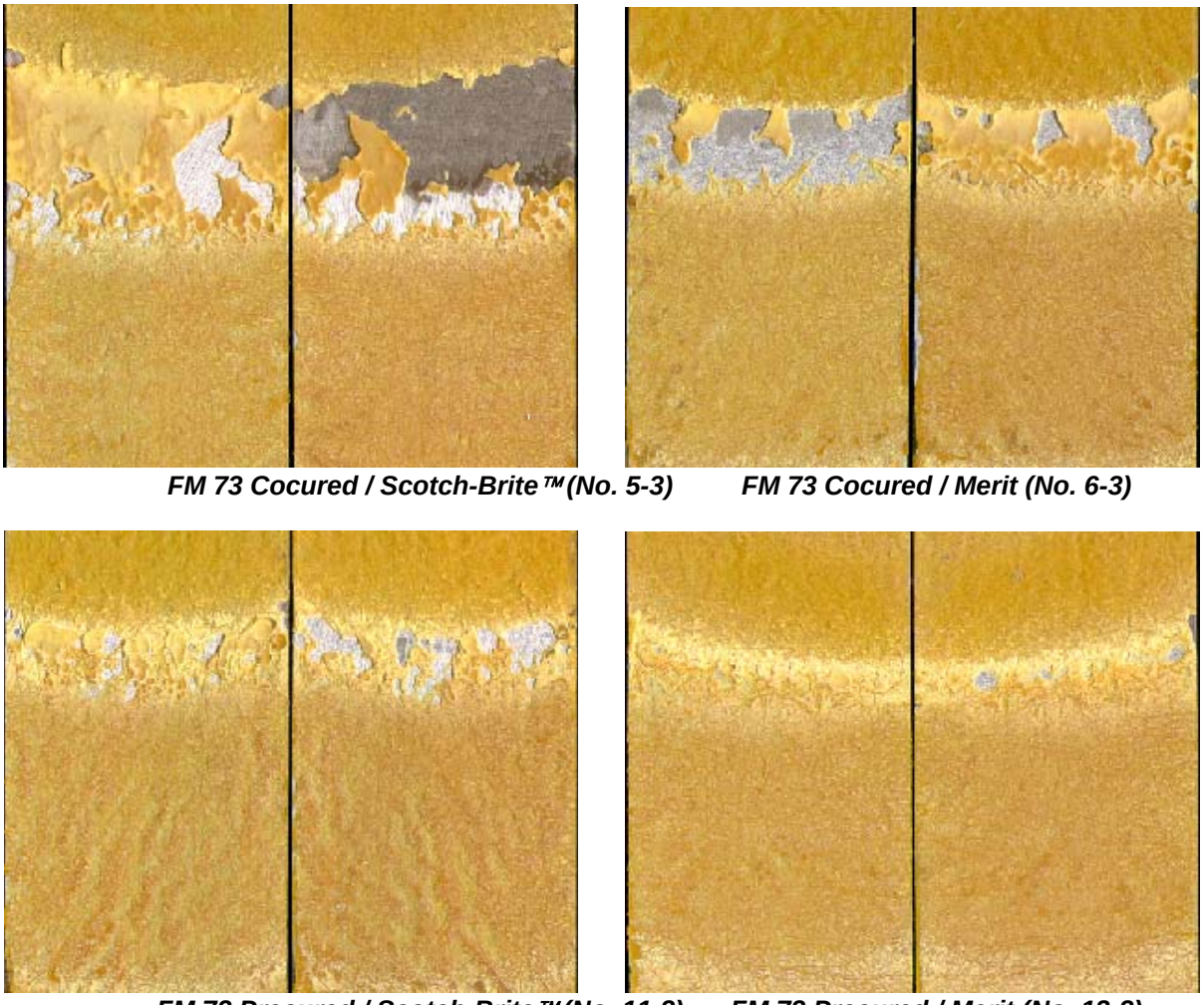


Figure 4.3-14 Failure mode photographs of lap shear specimens for primer cocure study

Representative specimens of the precured FM 73 adhesive are shown in Figure 4.3-15. Close examination shows failure at the metal surface for the Scotch-Brite™ specimens. The Merit 180 specimen has adhesive remaining over most of the crack growth area in the precured specimen.



FM 73 Cocured / Scotch-Brite™(No. 5-3) ***FM 73 Cocured / Merit (No. 6-3)***

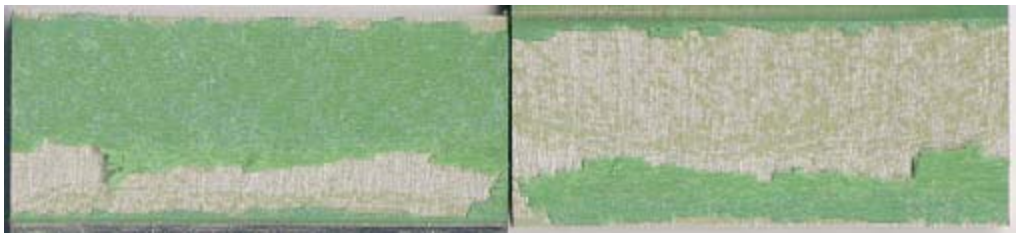
FM 73 Precured / Scotch-Brite™(No. 11-3) ***FM 73 Precured / Merit (No. 12-3)***

Figure 4.3-15 Failure modes for cocure study FM 73 wedge test specimens

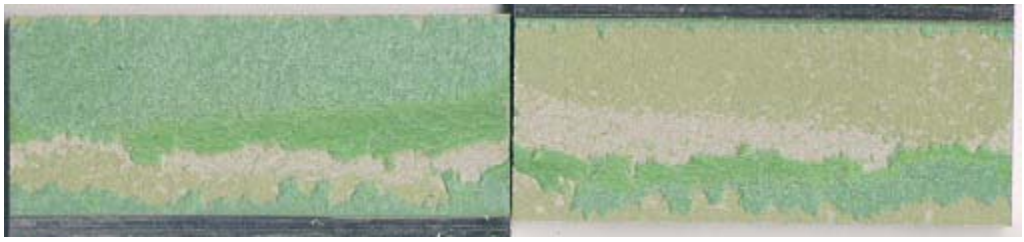
The EA 9696 and FM 300 adhesives did not show as significant of a difference in the performance and failure modes between the precured and cocured specimens or between the Scotch-Brite™ and Merit 180 abraded specimens in wedge testing.

In lap shear testing, FM 300 was the adhesive that showed significant differences in performance between the precured and cocured specimens. The cocured specimens had shear strengths of 1900 and 2200 psi for the Scotch-Brite™ and Merit abrasives respectively, and the precured had shear strengths of 4700 and 4600 psi for the Scotch-Brite™ and Merit abrasives respectively.

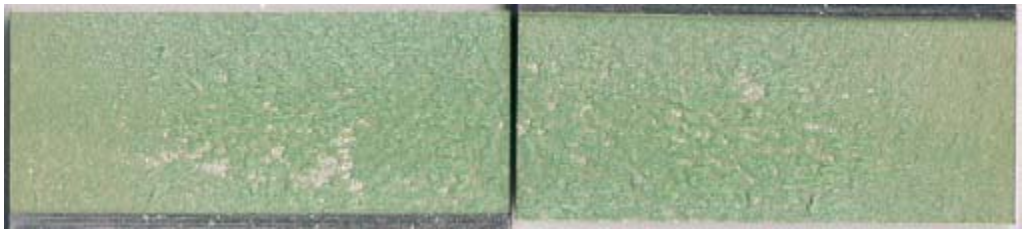
The FM 300 failure modes were hard to determine. There seemed to be a thin film of adhesive left on some of the metal surface of the cocured specimens, indicating a type of cohesive failure. The precured specimens showed a more traditional type of cohesive failure, although small mottled patches of bare metal can be seen. See Figure 4.3-16.



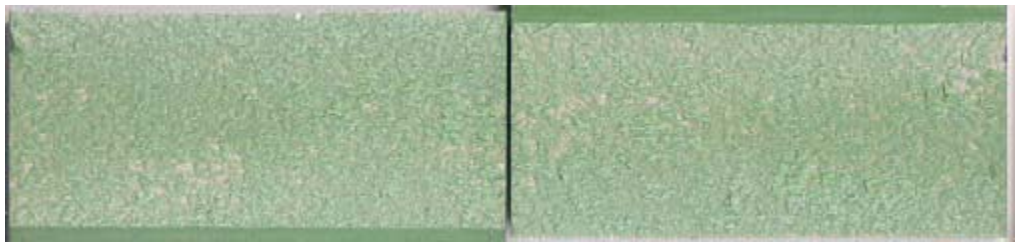
FM 300 Cocured / Scotch-Brite ™(Specimen No. 3-2)



FM 300 Cocured / Merit sandpaper (Specimen No. 4-2)



FM 300 Precured / Scotch-Brite ™(Specimen No. 9-2)



FM 300 Precured / Merit sandpaper (Specimen No. 10-2)

Figure 4.3-16 FM 300 lap shear failure modes for primer cocure study

For FM 73, the color of the adhesive was darker in the cocured lap shear specimens than in the precured lap shear specimens (Figure 4.3-14). This color difference was not present in the wedge test specimens. The cocured lap shear specimens showed a slight increase in cohesive failure over the precured specimens, but there was no significant difference in shear strength between the two cure modes.

The EA 9696 failure modes were surprising. These specimens had the highest shear strength numbers yet they exhibited 0 percent cohesive failure. All the EA 9696 specimens failed in the same way. Adhesive remained along the outer edge, with a small band of primer in the middle, then turning into a blend of primer and bare metal. See Figure 4.3-17.

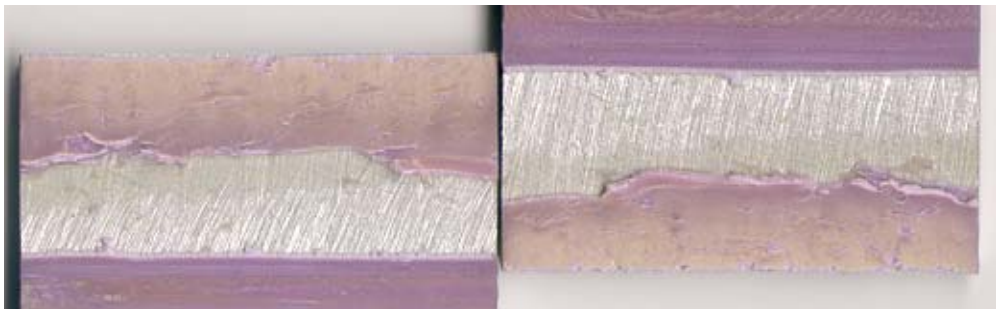
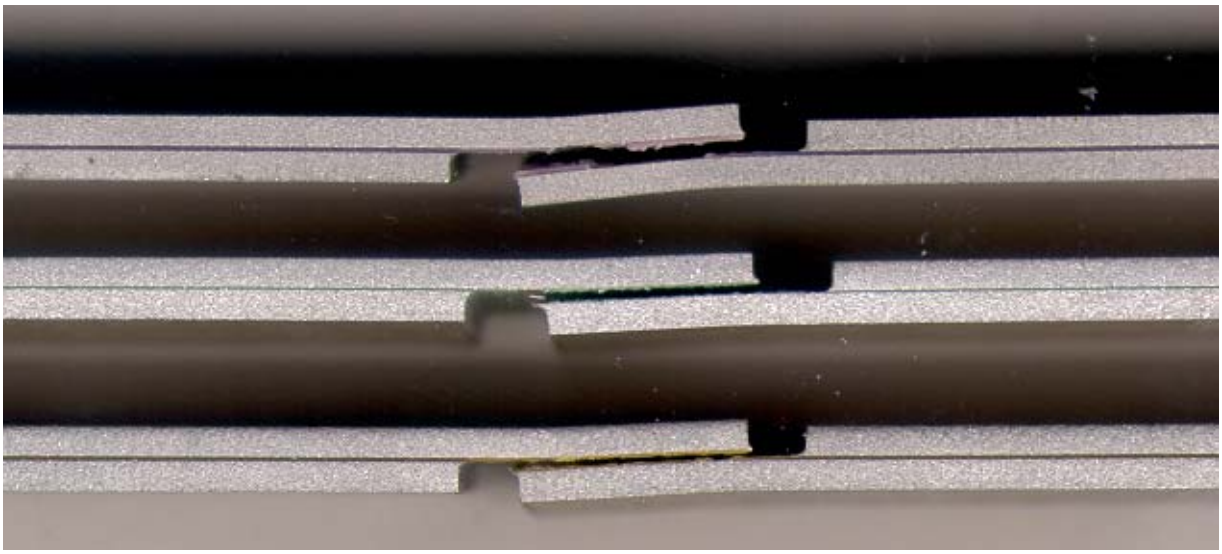


Figure 4.3-17 EA 9696 Cocured Scotch-Brite™ (Specimen No. 1-2)

The EA 9696 lap shear specimens also exhibited the most deformation of the aluminum adherends during the lap shear test (Figure 4.3-18). The strength of the adhesive was too great for the lap shear configuration of BSS7202. Peeling and bending forces were introduced as the aluminum deformed. This is the most likely explanation for the observed EA 9696 failure mode. To understand the actual surface preparation issues and interfacial relationships, thicker adherends should be used. Use of a smaller overlap area, perhaps ¼ square inch instead of ½ square inch is another possibility.



EA 9696 (top), FM 300 (middle), FM 73 (bottom)

Figure 4.3-18 Deformation in EA 9696 lap shear test specimens

In summary, the effects of cocuring or precuring BR 6747-1 bond primer applied over Boegel-EPII with the adhesives studied were most dependent on the adhesive chosen. The effect was exacerbated when certain surface preparation techniques were employed. FM 73 cocured wedge test specimens performed poorly compared to the precured specimens but showed little difference in lap shear testing. FM 300 cocured lap shear specimens performed poorly compared to the precured specimens but showed little difference in the wedge test. EA 9696 exhibited consistent performance between the cocured and precured methods in both lap shear and wedge testing.

The method of abrasion also has a small effect on the adhesive bond. Most cases showed there was less than 10% difference between the failure modes of the abrasive sandpaper and abrasive nylon pad within each test set. The notable exception was the precured wedge test specimens using FM 73. This test set showed 0% cohesive failure for the Scotch-Brite™ and 90% cohesive failure for the Merit. The adhesive failures in these specimens were at the primer/metal interface.

4.3.3 Alternate Adhesive Bond Primer Testing

3M Primer Candidates:

As new candidate environmentally-compliant, low volatile organic compound, adhesive bond primers became available, they were tested for compatibility in conjunction with the baseline sol-gel process in order to enable qualification of a second source low-VOC compliant bond primer product.

Recently, 3M made a number of improvements to their bond primer formulation which have resulted in very good properties when used in conjunction with phosphoric acid anodize aluminum surface preparation. The compatibility of these primers with the Boegel-EPII surface chemistry was assessed. Two of the recent developmental candidates, AMD269 and AMD271, were tested on aluminum 2024-T3 bare alloy and Ti-6Al-4V alloy. Aluminum alloy test specimens were grit-blasted with #180 alumina grit. In the case of titanium, the substrates were grit-blasted and subsequently immersion-treated at 190°F in a Turco 5578 alkaline solution for 15 minutes and then rinsed. The specimens were then spray-coated with Boegel-EPII and primed with the candidate primer. Two curing conditions were evaluated: 1) precuring the primer using the given manufacturer recommended conditions of 90 minutes at 250°F, and 2) cocuring by ambient drying of the primer with no additional curing prior to the film adhesive application and cure. In this method, the primer was cured at the same time as the adhesive system. The specimens were layed up with 3M AF 163-2M OST adhesive and cured. Wedge test specimens per ASTM D 3752 and climbing drum peel specimens per BSS7202 were fabricated and tested. Wedge test results are shown in Table 4.3-10 and Figure 4.3-19. Peel results are shown in Table 4.3-11 and Figure 4.3-20.

Table 4.3-10 Wedge Test Data for 3M Primer Candidates

Substrate	Primer & Cure	Crack Length (inch) after Exposure to 140F & > 98% RH (hours)							
		0	24	168	336	504	672	840	1000
1 aluminum	AMD 269 precure	1.19	1.33	1.33	1.55	1.56	1.60	1.60	1.66
2 aluminum	AMD 269 cocure	1.24	1.39	1.44	1.52	1.64	1.66	1.67	1.70
3 aluminum	AMD 271 precure	1.17	1.54	1.60	2.09	2.23	2.33	2.41	2.41
4 aluminum	AMD 271 cocure	1.27	1.39	1.54	2.19	2.38	2.42	2.52	2.52
5 titanium	AMD 269 precure	0.74	1.00	1.07	1.31	1.38	1.41	1.43	1.45
6 titanium	AMD 269 cocure	0.82	1.00	1.12	1.16	1.19	1.20	1.25	1.25
7 titanium	AMD 271 precure	0.76	1.07	1.19	1.40	1.48	1.53	1.54	1.54
8 titanium	AMD 271 cocure	0.76	0.94	1.03	1.15	1.22	1.29	1.33	1.33

*Failures on all the titanium panels were between the adhesive and primer. There was no bare metal showing.
**Failures on the aluminum were between the primer/sol-gel or primer/adhesive.

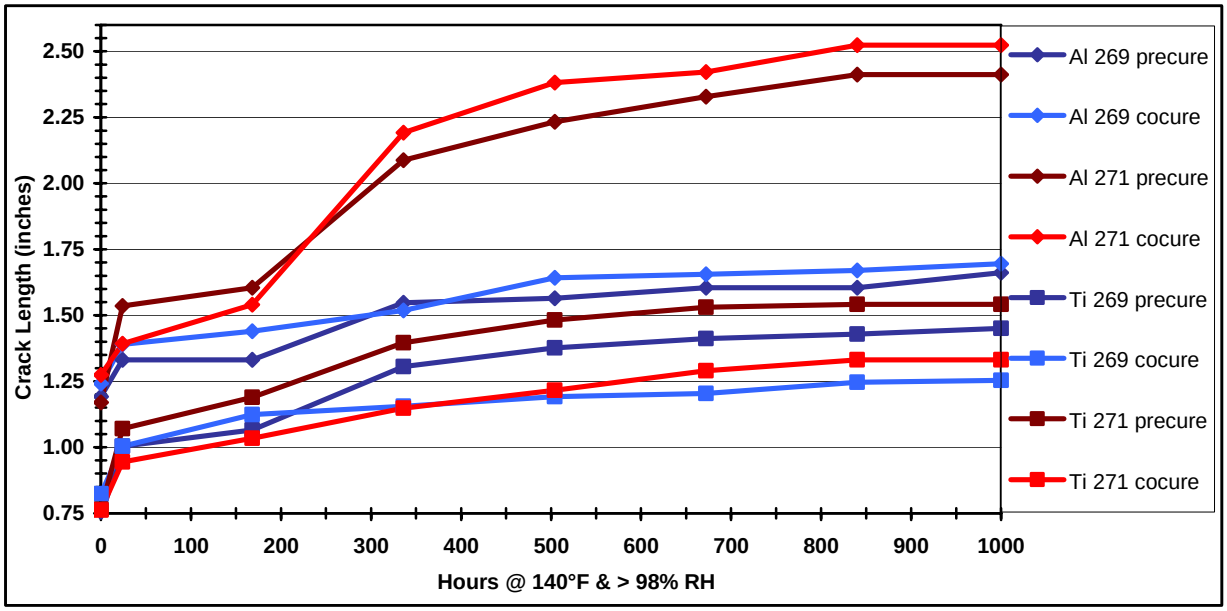


Figure 4.3-19 Wedge test crack growth for Boegel-EPII treated metal specimens with candidate 3M adhesive bond primers.

The data indicate the failure mode for the titanium panels was between the adhesive and primer, and the failure mode for the aluminum panels was a mixture of adhesive failure at the adhesive-primer and primer-sol-gel interfaces. The AMD 271 candidate did not perform well on aluminum and was marginal on titanium with regards to its wedge test behavior. The AMD 269

candidate generally performed better. There was no clear trend with regard to cocuring or procuring the primer in this system.

Table 4.3-11 Climbing Drum Peel Data for Candidate 3M Adhesive Bond Primers

Substrate	Primer & Cure	Peel Strength		% Coh Fail
		lb/inch	St.Dev.	
1 aluminum	AMD 269 precure	78	2.3	100
2 aluminum	AMD 269 cocure	85	3.4	100
3 aluminum	AMD 271 precure	84	7.0	100
4 aluminum	AMD 271 cocure	72	6.6	100

Substrate	Primer & Cure	Peel Strength		% Coh Fail
		lb/inch	St.Dev.	
5 titanium	AMD 269 precure	46	5.9	100
6 titanium	AMD 269 cocure	43	3.0	100
7 titanium	AMD 271 precure	51	3.0	100
8 titanium	AMD 271 cocure	47	4.0	100

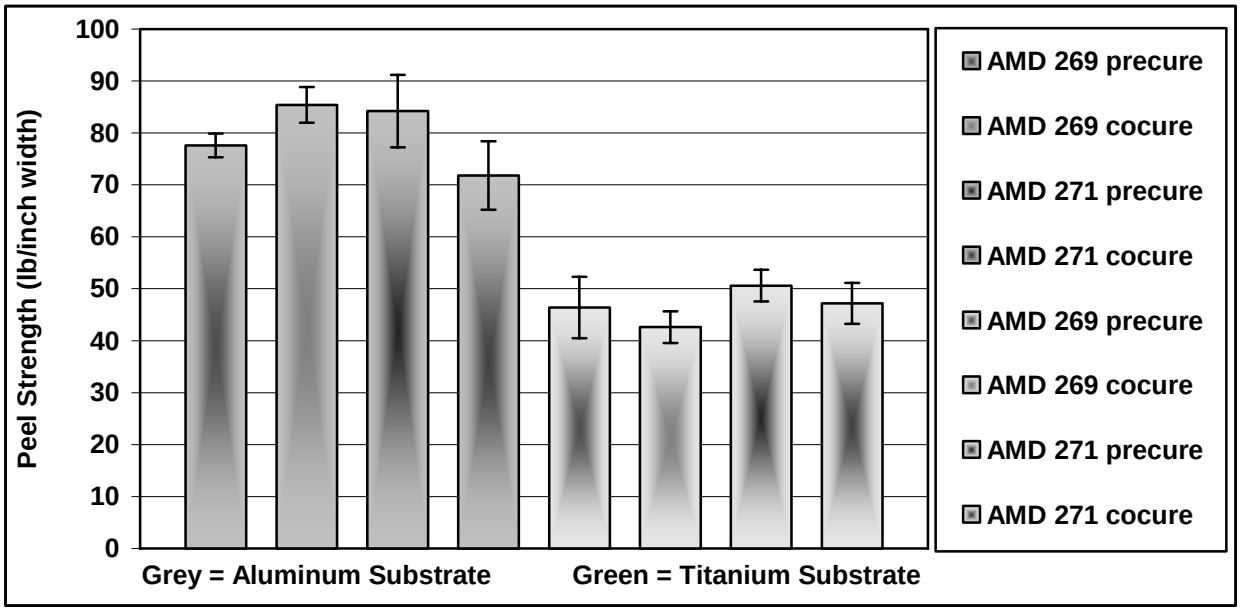


Figure 4.3-20 Climbing drum peel data for candidate 3M adhesive bond primers

4.3.4 3M Candidates, Adhesive Primer Testing

A second generation of the compliant adhesive primer candidates from 3M were evaluated over aluminum and titanium treated with Boegel-EPII. The EW 5000 primer was being assessed as a candidate for BMS5-89 and BMS5-137[17] adhesive primer specifications. Two new laboratory batches of this primer were received: These were designated as AMD 327 and AMD 328, and were essentially equivalent in chemistry with small changes in cosolvent to promote wetting on the surface. Data showed these primers gave good durability with a phosphoric acid anodize (PAA) surface on aluminum. The primer candidate chosen for this test, the AMD 327 variant.

To determine the performance of this primer with the sol-gel surface chemistry, several specimens were fabricated and sprayed with the candidate primer at the same time as the PAA-treated specimens. Both aluminum alloy and titanium alloy specimens were prepared by cleaning, degreasing, and grit-blasting the surface of the test panels with #180 alumina grit. , The primer was cured onto the surface at 260°F for 60 minutes. The dry film thickness was measured at 0.0003 in. Specimens were bonded, according to Table 4.3-12, with AF 163-2OST adhesive and cured in an autoclave. Test data are reported in Table 4.3-13 and Table 4.3-14 and Figure 4.3-21 and Figure 4.3-22.

Table 4.3-12 3M Primer EW 5000 (AMD 327 Variant) Test Matrix

Panel #	Alloy	Surface Prep	Primer	Test
1a	Ti-6Al-4V	Degrease, clean, #180 alumina grit-blast, Boegel-EPII with surfactant	3M EW 5000 /AMD 327	Wedge Test; ASTM D 3762
1b	Ti-6Al-4V	"	3M EW 5000 /AMD 327	CDP; BSS7206
1c	Ti-6Al-4V	"	3M EW 5000 /AMD 327	Lap Shear BSS7202
2a	2024-T3 Al bare	"	3M EW 5000 /AMD 327	Wedge Test; ASTM D 3762
2b	2024-T3 Al bare	"	3M EW 5000 /AMD 327	CDP; BSS7206
2c	2024-T3 Al bare	"	3M EW 5000 /AMD 327	Lap Shear BSS7202

Table 4.3-13 3M Primer EW 5000 (AMD 327) Lap Shear and Peel Test Results

Substrate	Shear Strength (psi)	Peel Strength (lb/inch)
Titanium - 1	7774	54.4
Titanium - 2	7556	61.0
Titanium - 3	7730	60.3
Titanium - 4	7782	66.3
Titanium - 5	7168	65.9
averages	**7602**	**61.6**
Std. Dev.	259	4.9

Substrate	Shear Strength (psi)	Peel Strength (lb/inch)
Aluminum - 1	6064	76.8
Aluminum - 2	5800	84.9
Aluminum - 3	5781	82.9
Aluminum - 4	5912	82.7
Aluminum - 5	5891	77.9
averages	**5890**	**81.0**
Std. Dev.	113	3.5

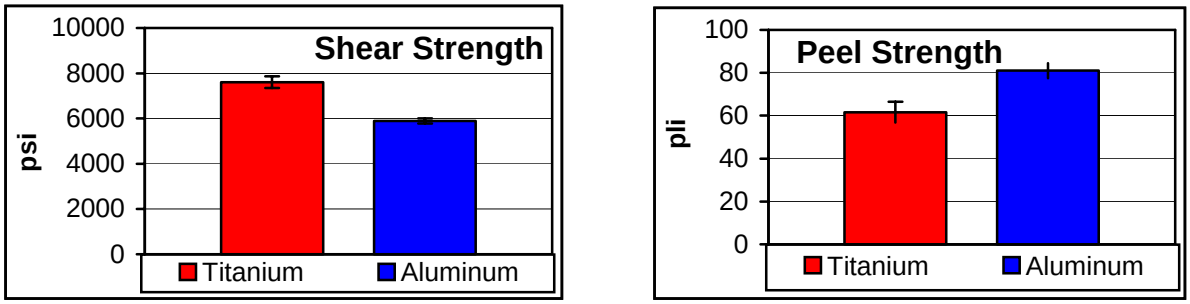


Figure 4.3-21 Lap shear and climbing drum peel data for 3M primer candidate, AMD 327

Lap shear and climbing drum peel tests were performed at ambient temperature per BSS7202 and BSS7206 respectively. Test results for the aluminum specimens exceeded the minimum requirements of the BMS 5-101 adhesive specification. The aluminum lap shear specimens exhibited an average of 74% cohesive failure within the adhesive. The titanium lap shear and peel tests performed well. There was 100% cohesive failure of the peel specimens and 97% cohesive failure on the lap shear specimens. Wedge test data for the bonded system is shown in Table 4.3-14 and Figure 4.3-22.

Table 4.3-14 3M Primer EW 5000 (AMD 327 Variant) Wedge Test Results

Specimen Number	Crack length (inch) after exposure to 140°F & >98% RH (hrs)						Crack Growth	Failure % Cohesive
	0	24	168	336	504	672		
Titanium-1	0.74	0.90	1.00	1.00	1.00	1.00	0.26	0
Titanium-2	0.70	0.87	1.07	1.07	1.07	1.07	0.37	0
Titanium-3	0.73	0.87	1.09	1.09	1.09	1.09	0.36	0
Titanium-4	0.74	0.90	1.16	1.16	1.16	1.16	0.42	0
Titanium-5	0.76	0.86	1.22	1.22	1.22	1.22	0.46	0
Average	0.73	0.88	1.11	1.11	1.11	1.11	0.37	0
Aluminum-1	1.11	1.24	1.34	1.34	1.34	1.34	0.23	76
Aluminum-2	1.18	1.35	1.35	1.38	1.38	1.38	0.20	60
Aluminum-3	1.26	1.41	1.61	1.61	1.61	1.61	0.35	50
Aluminum-4	1.12	1.23	1.31	1.31	1.31	1.31	0.19	60
Aluminum-5	1.05	1.19	1.28	1.28	1.28	1.28	0.23	60
Average	1.14	1.28	1.38	1.38	1.38	1.38	0.24	61

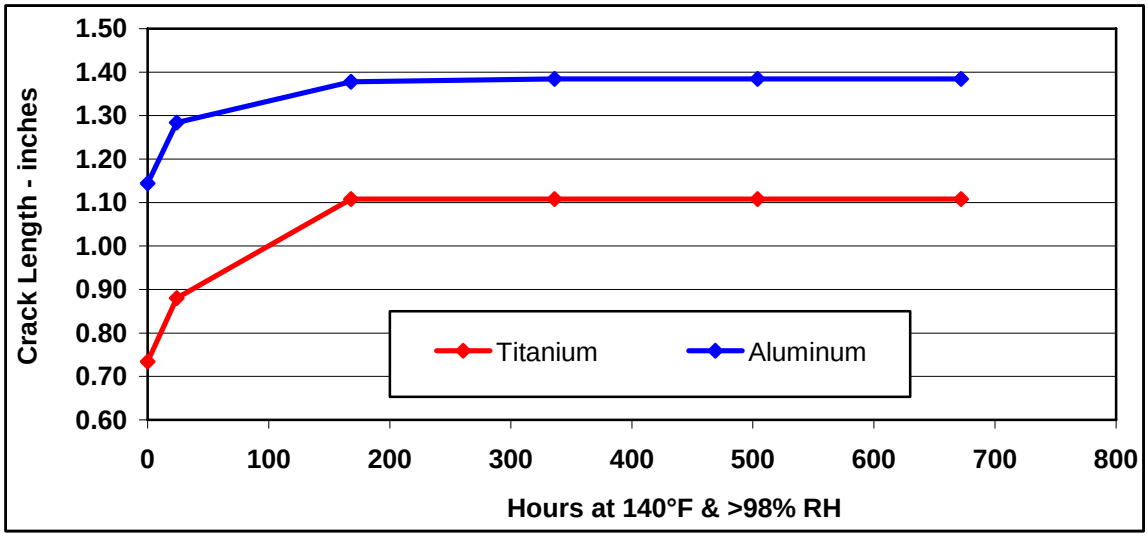


Figure 4.3-22 Wedge test data for EW 5000 (AMD 327 Variant) candidate

Wedge crack extension testing was performed per ASTM D 3762-98. The specimens were exposed to 140 degrees Fahrenheit and greater than 98% relative humidity. Wedge test results

were poorer than expected. The titanium specimens showed 100% adhesive failure, and the aluminum specimens showed approximately 40% adhesive failure.

4.3.5 Sovereign Adhesives (Henkel) Primer Candidate

An environmentally-compliant adhesive bond primer candidate, Sovereign AL 2000, was evaluated as a potential replacement for the high-VOC version BMS5-42[18], (350°F-cure nitrile phenolic adhesive system). The 3M EC 1660 primer was used as the control for this testing. Titanium alloy substrates were used and prepared per BSPS-07-001.[19] The pretreatment used in this study was where the titanium was prepared by first grit-blasting with #180 alumina grit, then conditioned by immersing in Turco 5578 at 190°F for 15 minutes, and finally coated with Boegel-EPII and dried under ambient conditions.

One set of specimens was primed with 3M EC 1660 by applying an approximately 0.00006 in coat of primer and curing at 350°F for one hour and then applying a second thin coat and cured at 230°F for 35 minutes to give a total primer thickness of 0.00011 in. For the AL 2000 primer, the coating was applied and cured per BMS5-42 for a total film thickness of 0.0005 in. This was slightly thicker than the supplier-recommended thickness. The test specimens were assembled using AF-30 Grade A (10 mil) nitrile-phenolic adhesive and cured at 350°F.

Wedge test data are shown in Table 4.3-15 and Figure 4.3-23. In general, the failure modes in the wedge test specimens for both primers were at the primer-to-adhesive interface, with the initial crack growth being slightly larger in the AL 2000 specimens.

Table 4.3-15 Wedge Test Data for BMS5-42 Primer Candidates

Primer	Crack Length (inch) after Exposure to 140°F & > 98% RH (hours)								% Coh. Fail
	0	24	168	336	504	672	840	1000	
EC 1660	0.89	0.96	0.96	1.03	1.08	1.11	1.11	1.12	0
AL 2000	0.83	1.16	1.16	1.16	1.16	1.18	1.18	1.18	0

*AL 2000 specimens exhibited primer to adhesive failure.

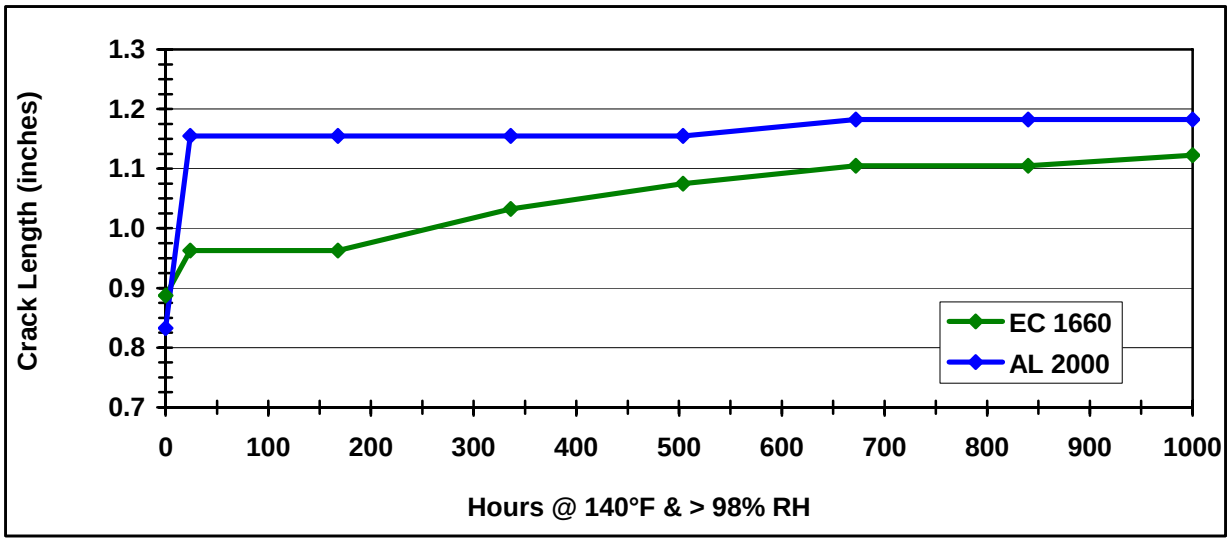


Figure 4.3-23 Wedge test data for BMS5-42 primer candidates

4.4 Kitting

4.4.1 First-Generation 2-Part Kit Development:

To significantly improve the ease of use of the sol-gel system, Boeing previously investigated precombining components of the sol-gel to reduce the number of separate components in a given "kit". This has several benefits, including reducing the potential for exposure of the moisture-sensitive elements to moisture, reducing the potential for spilling or improper mixing of the formulation, and reducing the number of components required in inventory. A two-part kit chemistry was devised and tested under laboratory conditions. In a two-component system, the (3-glycidoxy propyl)-trimethoxysilane (GTMS) was packaged as one component and the zirconium isopropoxide (TPOZ), glacial acetic acid (GAA) and water was mixed together and packaged as the second component..

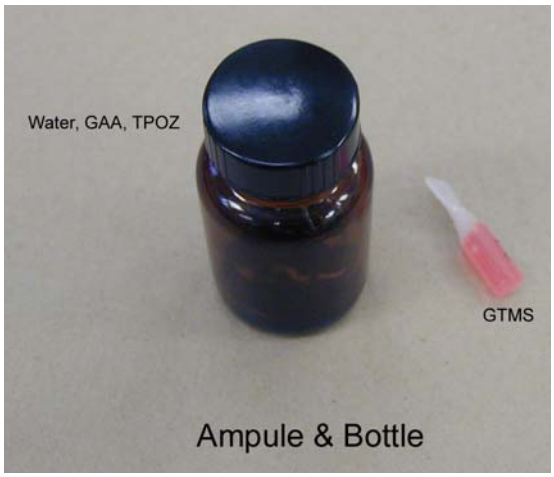
In this phase of study, the stability of the kit components was evaluated in different packaging schemes. Additionally, the ease of use of the various packaging schemes and durability under expected storage conditions was assessed.

Based on input from users and Boeing, AC Tech identified a number of candidate kit packaging configurations that could be used in a two-part kit configuration. These configurations are summarized in Table 4.4-1. Photographs of the packaging concepts are shown in Figure 4.4-1:

Table 4.4-1 Candidate Two-Part Sol-Gel Kit Packaging Configurations

Kit Config #	Description	Pros	Cons	Comments
1	Alodine-type Pen	Users are familiar with this configuration. Easy for brush-on techniques	Currently one-part; would have to be redesigned for a two-part	Configuration may be patent-controlled
2	Ampoule and Bottle	Small ampoule	May be difficult to get all of the GTMS out of the ampoule; could spill component	Ampoule could be taped to bottle to prevent loss
3	Blister Pack	No exposure to chemicals, self-contained until mixed, components spill-proof	Difficult to pour, may need to incorporate spout	Need to assess package handling durability and use
4	Double Syringe	Convenient, all parts attached so cannot be separated or lost	Would need to add alcohol to GTMS to make volumes comparable; have to figure out mixing;	Needs vessel to put solution into
5	Glass Ampoule	Very convenient for small repairs needing <1 oz of sol-gel; self-contained until mixed, components spill-proof	Size limited, probably only useful for <2 fluid oz of material	Filter on top filters out glass shards from breaking of membrane between components
6	Insert and Bottle	Convenient, all parts attached so cannot be separated or lost	Material on back of smaller insert can get lost or contaminated, could spill one component	With further development, could have plunger which would deploy through top insert and simplify kit
7	Liquid Sem-Kit	Improves on dispensing of syringe components	Complex; lots of packaging for perhaps small return	Current materials typically contain excess plasticizer; would need to assure new materials are clean
8	Syringe and Bottle	Relatively simple packaging scheme	Syringe deployment has been problematic in the past with spillage	
9	Tube and Bottle	Relatively simple packaging scheme	Degree of dispensation of material from bottle; could spill one component	
10	Two-Bottle Kit	Simple	Could spill one component	Useful for larger sizes

a. Kit Configuration #1-Alodine Pen



b..Kit Configuration #2-Ampule and Bottle

c. Kit Configuration #3-Blister Pack

d. Kit Configuration #10-Two-Bottle Kit

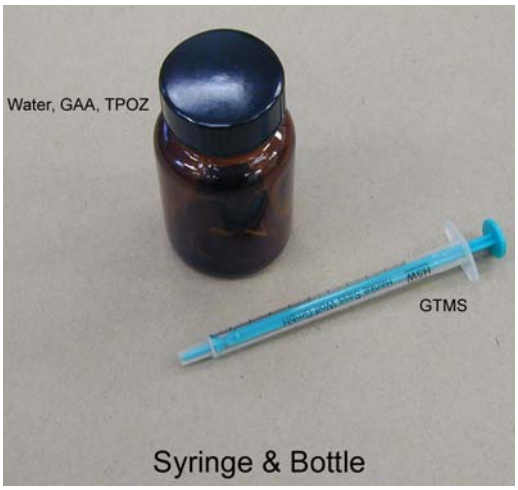
e. Kit Configuration #4-Double Syringe

f. Kit Configuration #5-Glass Ampoule

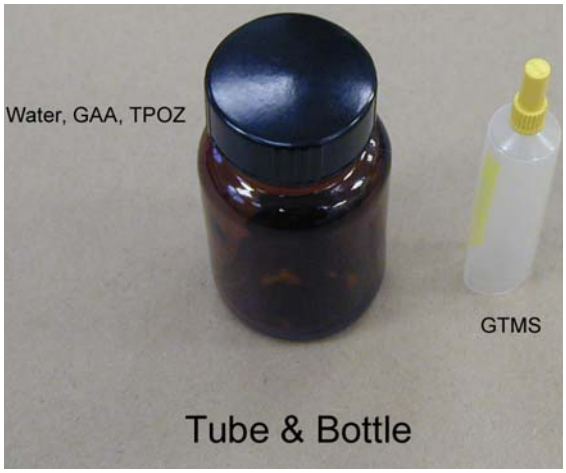
Figure 4.4-1 Photos a-f show proposed kit packaging configurations

g. Kit Configuration #6-Insert and Bottle

h. Kit Configuration #7-Liquid Sem-Kit



i. Kit Configuration #8- Syringe and Bottle



j. Kit Configuration #9-Tube and Bottle

Figure 4.4-1-cont'd Photos g-j show proposed kit packaging configurations

A survey was sent throughout the user-community to obtain feedback regarding the potential use of these packages and preferences for repair applications. The survey showed that a two-part blister-pack or a two-part bottle configuration was favored for ease of use. The two-part blister pack would have the advantage of being stored all in one place, so neither of the kit components could be separated and lost. Additionally, by removing the center separator, the mixing would be accomplished without any potential spilling or exposure to chemicals.

Alternatively, the two-part bottle kit was favored because of its simplicity. Both configurations were deemed worthy of further testing. The glass ampoule kits had the same advantage as the blister pack and were originally included in the test matrix. There were difficulties in finding a vendor to fill the glass ampoules and they were later dropped from the test matrix.

Aging testing consisted of ambient-temperature aging of the kits and accelerated aging of the kits in a warm and moist environment. Initially, the plan was to verify a 6-month shelf-life for adhesive bonding and also painting applications. Verification testing consisted of bond

performance and moisture durability testing as well as analytical testing to ascertain whether any chemical aging effects had occurred in the two components over time and also to determine whether the kit packaging caused any contamination issues.

Kit orders were placed with AC Tech for the 2-part sol-gel kits, as described in Table 4.4-2. The number of kits and batching requirements are shown in the table. Four-part syringe kits (the existing small kit configuration) were included as controls.

Table 4.4-2 Two-Part Sol-Gel Kit Orders

Two-Part Sol-Gel Kits						
Batch No.	Kit Configuration	Air Force (Mazza)	Navy (Tillman)	Army (DePiero)	Boeing (Blohowiak)	TOTAL
1	2 oz Blister Packs with surfactant	45			16	61
1	2 oz Blister Packs without surfactant					0
1	2 oz Ampoule Kits with surfactant	45				45
1	2 oz Ampoule Kits without surfactant					0
1	2 oz Bottle Kits with surfactant	80		4	32	116
1	2 oz Bottle Kits without surfactant	50		4		54
1	100 ml Standard Kit (4-part syringe & bottle)	25				25
2	2 oz Blister Packs with surfactant		80	10	16	106
2	2 oz Blister Packs without surfactant		120	10		130
2	2 oz Ampoule Kits with surfactant			10		10
2	2 oz Ampoule Kits without surfactant			10		10
2	2 oz Bottle Kits with surfactant	20		10	32	62
2	2 oz Bottle Kits without surfactant			10		10
2	100 ml Standard Kit (4-part syringe & bottle)		12			12
3	2 oz Blister Packs with surfactant				65	65
3	2 oz Blister Packs without surfactant					0
3	2 oz Ampoule Kits with surfactant				40	40
3	2 oz Ampoule Kits without surfactant					0
3	2 oz Bottle Kits with surfactant	20		4	56	80
3	2 oz Bottle Kits without surfactant			4		4
3	100 ml Standard Kit (4-part syringe & bottle)				16	16
	TOTALS	285	212	76	273	846

Two-part kits were received from AC Tech in late October 2003. Three batches each of bottle and blister packs plus one batch of the standard four-part control kit were received.

Analytical tests showed a problem with the kit contents. Inductively Coupled Plasma (ICP) analysis of metal content detected a lack of the zirconium component in all 3 batches of the bottle kits, as shown in Table 4.4-3.

Table 4.4-3 ICP Analysis of Two-Part Kit Components

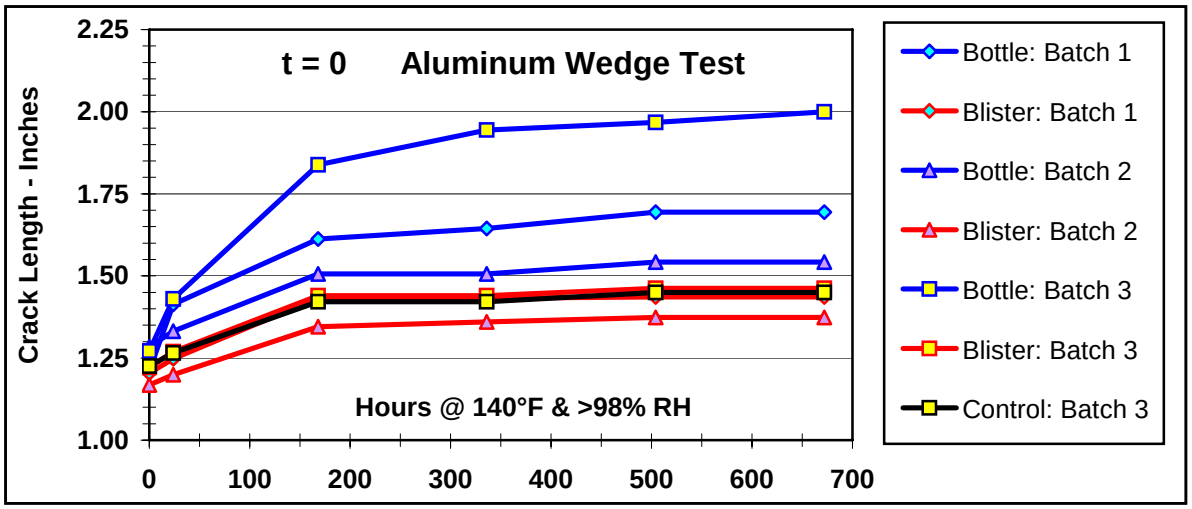
Batch No.	Type		Part A (Silane)				Part B (Aqueous)			
			Si ppm	Na ppm	S ppm		Si ppm	Na ppm	S ppm	Zr ppm
1	Bottle		123700	135	33		<0.1	14	0.4	12
2	Bottle		133700	111	37		0.2	26	0.5	19
3	Bottle		156000	12	19		<0.1	29	0.5	19
3	Blister		116000	31	24		24	19	1.3	1881

Theoretically, the concentration of Zr should be 2090 ppm in part B (the aqueous portion), given that the zirconium n-propoxide (TPOZ) concentration is one percent of the total kit and that zirconium makes up 20.5 percent of TPOZ. AC Tech reported the vessel used to mix the aqueous portion contained a large amount of white precipitate after disbursement of the zirconium aliquots into the kits. This is presumably the missing zirconium complex.

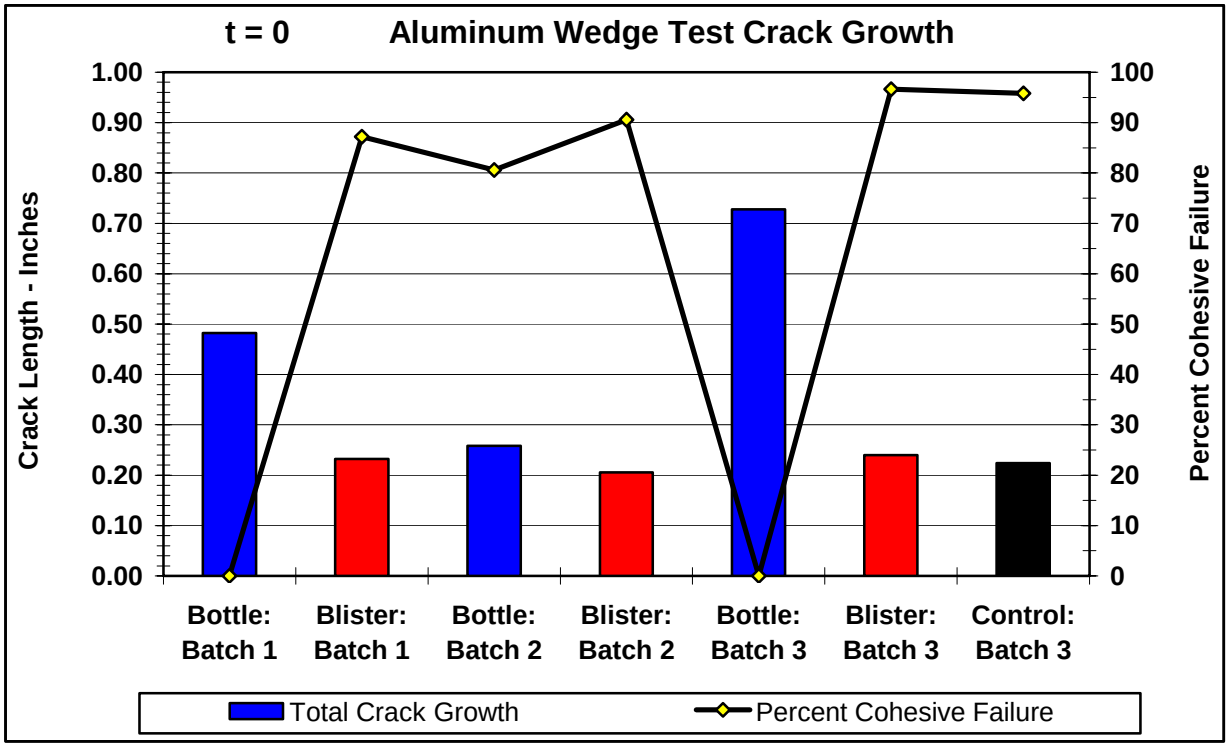
The ICP analysis also confirmed a leakage problem with the blister packs. The blister pack analyzed showed 24 ppm of silicon had migrated into Part B from Part A. Kits stored at elevated temperatures (at the Navy location) showed a greater degree of migration between the two sections of the blister pack. The packs analyzed at Boeing were all stored at room temperature, but still showed a leakage and migration problem.

Performance tests were started in mid November 2003. This group of tests was intended to determine the initial, baseline performance and was termed “t = 0” or time zero. For clarification, time zero was denoted as the start of the test, not the moment when the kits were first made. Performance testing consisted of wedge crack extension and peel tests on aluminum and titanium substrates. Test specimens were assembled using AF 163-2 OST, Grade 10 film adhesive. Figure 4.4-2 shows the results of the aluminum wedge tests. Figure 4.4-3 shows the results for the titanium wedge test specimens. Figure 4.4-4 shows the peel test results for both aluminum and titanium substrates.

A second set of aluminum test specimens was made in mid December, at t = 1 month, in accordance with the test matrix. This was about the same time the zirconium problem was discovered. It was decided to halt all testing at this time because of leakage in the blister packs and the lack of zirconium in the bottle kits.

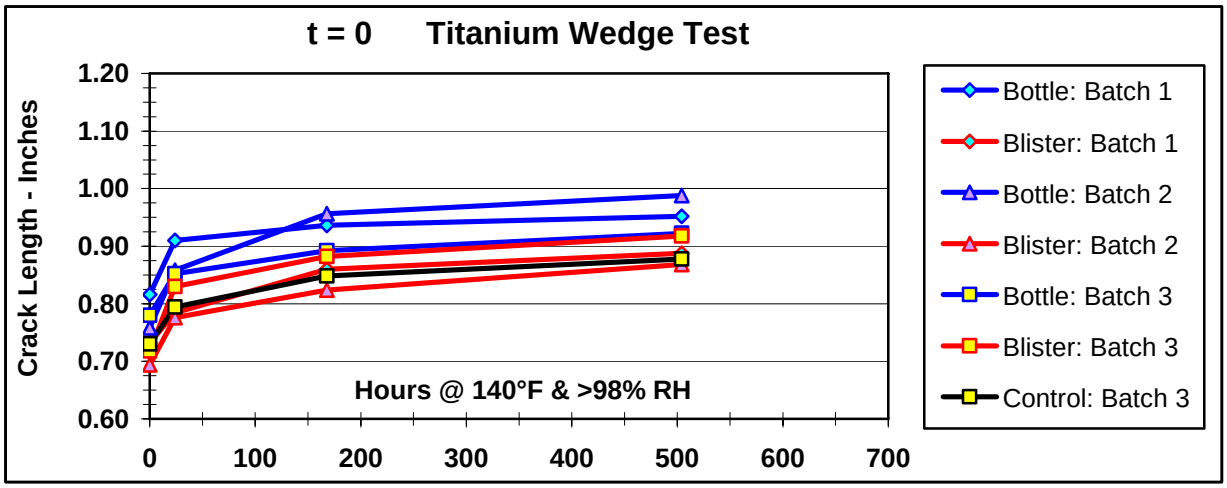


Key: ***blue lines = bottle kits, red lines = blister kits, black line = control (std. 4-part kit)***
blue points = batch 1, violet points = batch 2, yellow points = batch 3



Key: ***blue bars = bottle kits, red bars = blister packs, black bar = control (std. 4-part kit)***

Figure 4.4-2 Aluminum wedge test results for Phase I kits



Key: ***blue lines = bottle kits, red lines = blister packs, black line = control (std. 4-part kit)***
blue points = batch 1, violet points = batch 2, yellow points = batch 3

Figure 4.4-3 Titanium wedge test results for 2-part kits

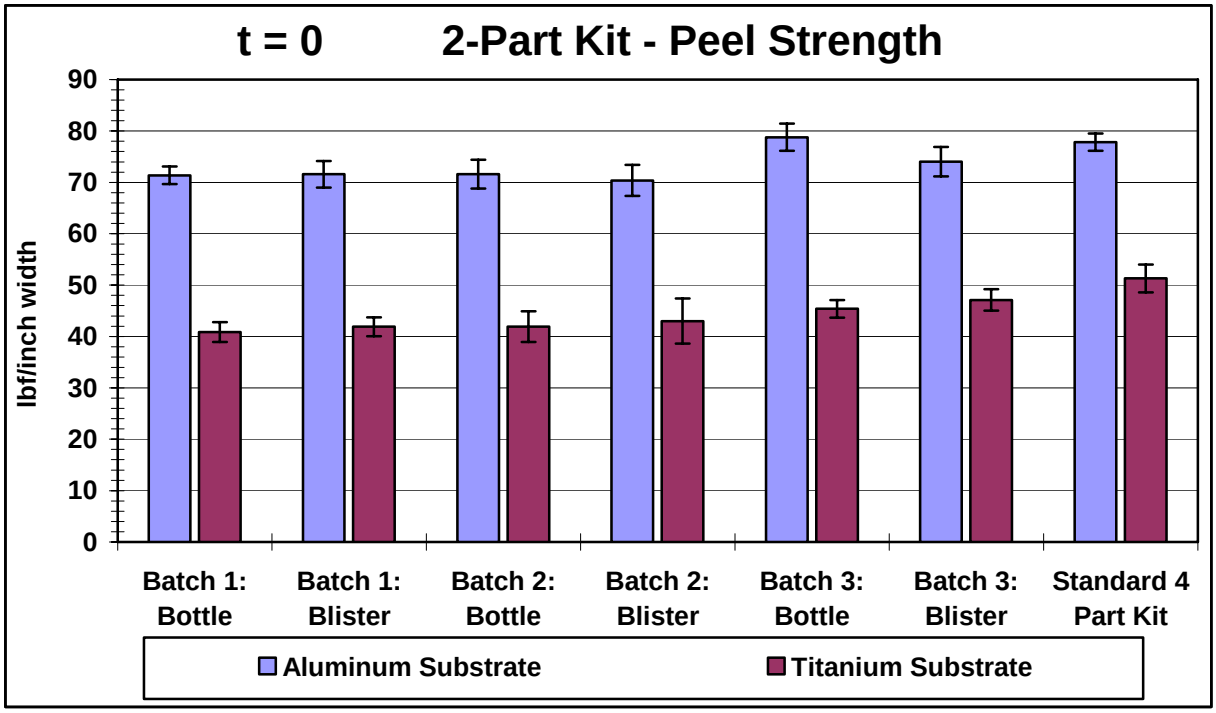


Figure 4.4-4 Peel test results for 2-part kits

The performance tests point out the importance of the zirconium component in the mixture for enhanced environmental durability. The aluminum wedge tests show the initial crack length, total crack growth, and degree of adhesive failure are all larger in the specimens that lack zirconium (bottle) than in the specimens that contain zirconium (blister pack and control). It is especially apparent in the specimens from Batch 1 and Batch 3. The Batch 2 specimens had a

larger initial crack length, but crack growth during exposure was about equal to that of the blister pack and control specimens. The Batch 2 bottle packs also showed a greater amount of cohesive failure than was shown by the Batch 1 and 3 bottle packs (80% vs. 0%).

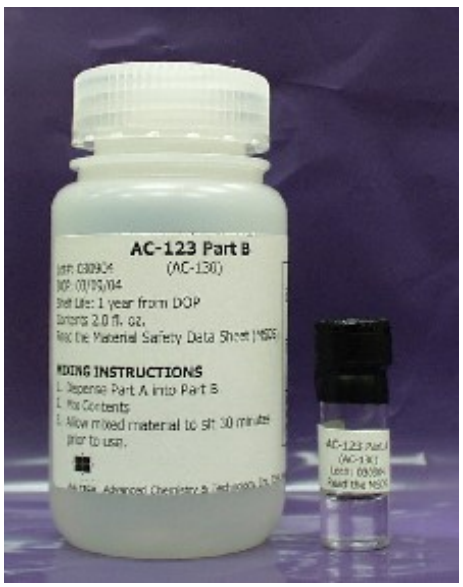
The titanium wedge test results demonstrated the same trend to a lesser degree for crack length and growth. It is noted that the titanium specimens used a much more robust surface pretreatment (grit-blasting) than the aluminum specimens (sanding) prior to sol-gel. Both substrate types were aqueous degreased and alkaline cleaned. The titanium substrates were then grit-blasted with 180-grit white aluminum oxide and treated with Boegel-EPII. The aluminum specimens were sanded using Merit 180 grit sandpaper using a random orbital sander and then treated with Boegel-EPII. This surface preparation of the aluminum was chosen because it is more sensitive to changes in performance and durability as the kits age.

The ambient temperature peel tests did not show any significant differences with or without zirconium. The failure mode for all the specimens was 100% cohesive.

4.4.2 Second-Generation 2-Park Kit Development: Twist-Tip Vials

Personnel from Boeing and AC Tech met at Boeing in Seattle on April 6, 2004 to discuss progress in the two-part sol-gel kit packaging. The second-generation kit configurations were packaged in the bottle packs shown in Figure 4.4-5. Leakage of components in the packages continued to be a problem during shipment. Leaks were discovered in both the large plastic bottle containing the aqueous mixture and the small glass bottle containing the silane component. Potential solutions to the leakage problem are bottle cap liners and/or some type of film seal over the open bottle.

AC Tech brought a third batch of AC-123 with them to the April meeting. These were bottle kits with a modified sem-kit-like injector mounted on the bottle top, as shown in Figure 4.4-5. The modification is heat-molded into the cap. The small tube mounted on the bottle top contains the silane. Using the supplied plunger, the operator can inject the silane directly into the bottle containing the aqueous mixture. The bottle top remains on the bottle during this procedure, so no spillage occurs. However, leakage around the seal of the silane tube to the bottle top occurred even during routine handling and movement, this was considered to be an unsolvable problem.



2-part bottle pack

2-part sem-kit pack

2-part MicroDose™ pack

Figure 4.4-5 Second-generation kit packaging configurations

AC Tech presented another alternative for packaging the silane portion. These are the MicroDose™ vials shown in Figure 4.4-5. These are sealed plastic vials, so leakage should not be a problem. The vials come in a variety of sizes, ranging from 0.2 to 15 milliliters. The vials themselves are available in low-density polyethylene (LDPE), an high-density polyethylene (HDPE)/LDPE blend, or polypropylene and they can be packaged under a nitrogen atmosphere. The MicroDose™ vials come with a tip that the operator must cut off. A Twist-Tip™ design is also available and, as the name implies, the tip is twisted off the vial. MicroDose™ and Twist-Tip™ vials are made by Unicep Packaging, Inc.

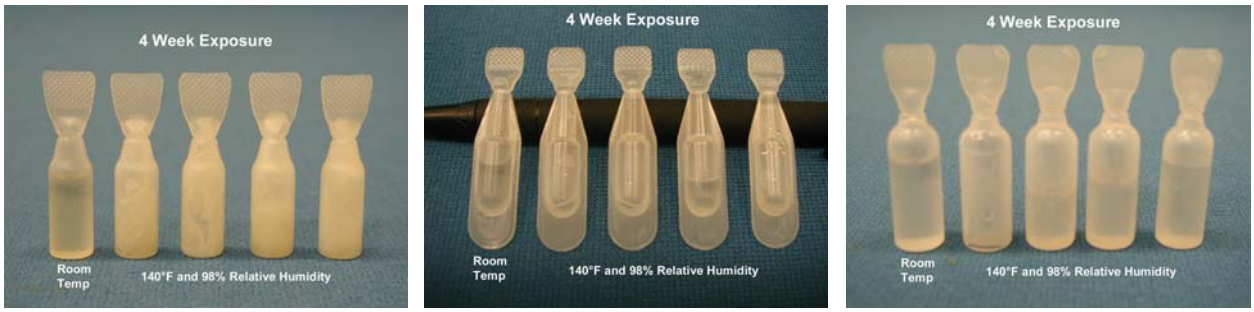
It was decided to go forward with the MicroDose™ and/or Twist-Tip™ concept. This type of package, if successful, could also replace the GTMS, TPOZ and GAA syringes currently in use with the smaller four-part kits. Information that needed to be determined included the residual volume left after dispensing and potential leaching of plasticizers from the vessels.

Also under continued consideration was a crushable ampoule-type configuration for use as a touch-up pen replacement. Figure 4.4-6 shows one example. This concept was tabled for further development under the limited scope of this project.

Figure 4.4-6 Two part crushable ampoule

Due to the mixing and leakage issues, it was decided that all the existing two-part kits at Boeing as of April 2004 would be destroyed. This included the original blister and bottle kits that were received in 2003 and the newer kits received in March and April 2004. The four-part kits received in 2003 as controls were kept and used as controls for the aging study.

In May 2004, AC Tech submitted Twist-Tip™ kits to Boeing for preliminary testing. The intention of the preliminary testing at Boeing was to accelerate the aging and determine if plasticizers or other components were leaching out of the LDPE packaging. Twist-Tip™ vials and glass control vials were stored in an environmental chamber at 140°F and 98% RH for four weeks. Gas chromatography measurements showed no contamination of the GTMS, GAA, or TPOZ from the plastic vials;. However, the vials leaked. After one week in the environmental chamber, white precipitates were observed in several of the TPOZ vials. After four weeks, all of the TPOZ component in the vials had decomposed such that it had completely precipitated (Figure 4.4-7). Additionally, material loss was observed in both the GAA and GTMS vials. Kits stored in an oven at 140°F showed loss of material but no TPOZ precipitation. Further testing revealed the vials were leaking at the flat end seal.



a. TPOZ ***b. GAA*** ***c. GTMS***

Figure 4.4-7 Twist-Tip™ vials after 4 weeks at 140°F and 98% RH

Due to the disappointing preliminary test results, personnel from Boeing and AC Tech met in Seattle on June 24th to discuss packaging options and ongoing quality control concerns. A detailed plan for identifying and testing packaging options was presented by AC Tech and approved by Boeing. Several variations of Twist-Tip™ packaging were evaluated, including different polymers and different sealing methods. The kits were subjected to hot/dry conditions (140°F oven), hot/wet conditions (100°F/95% RH or 95°F/85% RH), and standard conditions (77°F/50% RH). Glass vials were used as the control packaging at each environmental condition. The stability of the kits was assessed by gas chromatography, fourier transform infrared spectroscopy, and peel and wedge performance testing.

Several configurations of Unicep vials were evaluated (Figure 4.4-8):

1) Twist-Tip™ Polypropylene

2) Twist-Tip™ Medium Density Polyethylene

3) MicroDose™ Medium Density Polyethylene

Figure 4.4-8 Unicep vials configurations (www.unicep.com)

All vials were packaged under nitrogen and the tips were heat sealed. Half of the vials were tested in sealed Mylar® bags and the other half were tested without bags. The kits were subjected to hot/dry conditions (140°F oven), hot/wet conditions (100°F/95% RH or 95°F/85% RH), and standard conditions (77°F/50% RH). Glass vials were used as the control packaging at each environmental condition.

After 1 week of hot/dry exposure and 4 weeks of hot/wet exposure, the bagged Twist-Tip™ polypropylene vials were the only ones that did not show significant weight loss for any of the materials (GAA, GTMS, TPOZ). Unfortunately, AC Tech subsequently discovered these vials were no longer an option for AC-130 components because Unicep decided it was not equipped for production-scale packaging of the chemicals involved.

As an alternative, AC Tech tested Nalgene Micro Packaging vials as candidates for AC-130 kits. The vials were nitrogen flushed during filling and placed in nitrogen-purged Mylar bags. As done previously, the kits were subjected to hot/dry conditions (140°F oven), hot/wet conditions (100°F/95% RH or 95°F/85% RH), and standard conditions (77°F/50% RH). Glass vials were used as the control packaging at each environmental condition. Preliminary results after one week of exposure indicated the packaging maintained its integrity under the different environmental conditions.

4.4.3 Navy Shipping Profile

The US Navy developed a worst-case temperature profile for the uncontrolled shipment of materials. The profile requires the kits to withstand exposure to 140°F for 2 weeks. Previous tests with the Twist-Tip™ vials showed leakage (evaporation) of materials at this temperature. There was some concern as to whether or not the existing 4-part syringe kits could meet this requirement. Also, the effect this temperature exposure has on performance tests was unknown.

Two tests were run to provide an answer to these questions and to provide a baseline against which the performance of the Nalgene Micro Packaging Vials could be measured. The first test

monitored weight changes in the components of AC-130 100 ml syringe kits at various temperatures and humidity levels. The second test was to perform peel and wedge crack tests using sol-gel ingredients that were stored at 140° F for 2 weeks. The sol-gel ingredients for the performance tests were stored in glass vials and were intended to serve as controls to determine if the elevated temperature is detrimental to any of the ingredients.

Four 100 ml kits of AC-130 from batch number 101003 were exposed to elevated-temperature conditions. Two kits were placed in a 140°F oven and two kits were placed in a 95°F / 85% relative humidity chamber. The kit components were removed from their cardboard packaging. The Mylar® pouches containing the individual syringes were left intact. The water component was contained in a 125 cc Nalgene bottle. Weight measurements were made initially, after one week exposure and after two weeks exposure. The gross weights included the weight of the Mylar® pouch, labels, syringe, and syringe contents. The Mylar® pouches were opened after the two week exposure, and the final volume remaining in each syringe was measured, using the markings on the syringe barrel. Any air bubbles that were present in the syringes were expelled before the volumes were measured. Volume measurements were not possible prior to temperature exposure because the Mylar® pouches were opaque and the pouches were sealed for the test exposure. Table 4.4-4 contains all the weight change data. The (initial) target volumes listed are the nominal fill volumes supplied by AC Tech.

Table 4.4-4 AC-130 Weight Change After Environmental Exposure

Kit No.	Contents	Exposure Environment	Initial Gross Wt. (grams)	1-week exposure Gross Wt.	2-week exposure Gross Wt.	1-week exposure Wt. change	2-week exposure Wt. change	Final Volume (ml)	(Initial) Target Volume
1	GTMS	140°F dry	9.0086	8.9951	8.9853	-0.0135	-0.0233	1.9	1.93
1	GAA	140°F dry	7.4696	7.4640	7.4632	-0.0056	-0.0064	0.3	0.43
1	TPOZ	140°F dry	8.0405	8.0336	8.0334	-0.0069	-0.0071	0.9	0.97
1	H2O	140°F dry	119.208	119.055	118.957	-0.153	-0.251	-	-
2	GTMS	140°F dry	8.9758	8.9676	8.9674	-0.0082	-0.0084	1.8	1.93
2	GAA	140°F dry	7.3384	7.2992	7.2567	-0.0392	-0.0817	0.1	0.43
2	TPOZ	140°F dry	8.0470	8.0399	8.0391	-0.0071	-0.0079	0.9	0.97
2	H2O	140°F dry	119.212	119.059	118.958	-0.153	-0.254	-	-
3	GTMS	95°F/85% RH	9.0574	9.0557	9.0560	-0.0017	-0.0014	1.9	1.93
3	GAA	95°F/85% RH	7.4007	7.3987	7.3978	-0.0020	-0.0029	0.2	0.43
3	TPOZ	95°F/85% RH	8.1267	8.1252	8.1246	-0.0015	-0.0021	1.0	0.97
3	H2O	95°F/85% RH	120.052	120.042	120.042	-0.010	-0.010	-	-
4	GTMS	95°F/85% RH	8.9998	9.0013	9.0040	0.0015	0.0042	1.9	1.93
4	GAA	95°F/85% RH	7.4047	7.4008	7.3972	-0.0039	-0.0075	0.25	0.43
4	TPOZ	95°F/85% RH	8.1881	8.1913	8.1919	0.0032	0.0038	1.0	0.97
4	H2O	95°F/85% RH	119.348	119.340	119.339	-0.008	-0.009	-	-

Several observations were made regarding the condition of the syringes after the two week exposure.

- All kits: No liquid was present outside the syringe. The inside of all the Mylar® packages were clean and dry.

- 3-glycidoxypropyltrimethoxysilane (GTMS): Samples exposed to 140°F had an air bubble present in the barrel of the syringe. Samples exposed to not/wet conditioning had a much smaller air bubble in the tip of the syringe only.
- Glacial acetic acid (GAA): An acetic acid odor was detected upon opening the Mylar® pack. All samples had an air bubble present in the barrel of the syringe. Both 140°F samples showed brown discoloration of the paper label on the exterior of the syringe. One hot/wet conditioned sample also had a discolored label, but not as severe.
- Zirconium n-propoxide (TPOZ): Samples exposed to 140°F had an air bubble present in the barrel of the syringe. Samples exposed to hot/wet conditioning had a much smaller air bubble in the tip of the syringe only. Samples exposed to 140°F were slightly darker than samples exposed to 95°F/85% RH. No crystallization was observed.

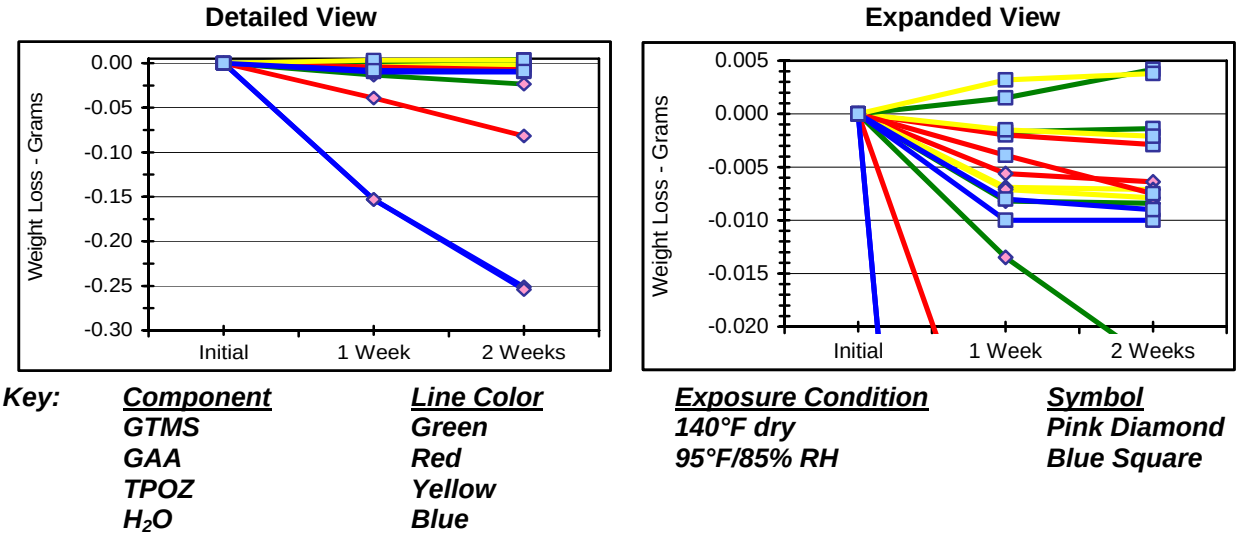


Figure 4.4-9 AC-130 kit component weight change after environmental exposure

Figure 4.4-9 shows the weight change data for all the kit components. Most components showed a net weight loss. Only two samples from the 95°F/85% RH exposure condition, one GTMS and one TPOZ syringe, showed net weight gains, and they were both less than 0.005 grams.

Most components, except the water, showed less than a 0.01 gram difference between the initial and final weight. One GTMS syringe exposed to 140°F lost 0.0233 grams and one GAA syringe exposed to 140°F lost 0.0817 grams. Both of the water bottles exposed to 95°F/85% RH lost 0.01 grams or less, and the two exposed to 140°F lost approximately 0.25 grams.

The kits exposed to 95°F/85% RH exhibited less change than those exposed to 140°F. This is not surprising. All the syringes did gain or lose weight, even though they were in sealed Mylar® pouches. Since there was no visible liquid present inside the Mylar® pouch, the sol-gel ingredients must have escaped as a vapor and have either passed through the Mylar® film or through the seal in the film. The latter choice seems to be more likely and it would explain the variation observed in the weight losses. The syringes that lost more weight were most likely sealed less tightly.

This test was only designed to measure weight change over the two week temperature exposure period. The comparison of the final volume to the target volume is included as additional information only. However, the results for GAA show reasons for concern. The final volume of GAA was significantly below the target volume in all cases. The amount of material lost ranged from 30% to over 75% of the original volume. This is too large an amount to be accounted for by this test. Other users of AC-130 syringe kits reported low volumes of GAA. The kits used in this test were approximately nine months old. GAA is either being lost as the kits age or there was an insufficient amount of GAA upon initial filling. Table 4.4-5 gives an estimate of the amount of GAA that was lost.

Table 4.4-5 Glacial Acetic Acid Losses Under High Temp Storage Conditions

Kit No.	Test Loss		Target Volume (ml)	Final Observed Volume (ml)	Total Volume Loss (ml)	Missing Volume (ml)
	Weight (grams)	Volume (ml)				
1	0.0064	0.0061	0.43	0.3	0.13	0.12
2	0.0817	0.078	0.43	0.1	0.33	0.25
3	0.0029	0.0028	0.43	0.2	0.23	0.23
4	0.0025	0.0023	0.43	0.25	0.18	0.18

The volume of GAA lost during the test was determined by dividing the measured weight loss by the relative density of GAA (1.0477 $^{g}/_{ml}$). The total volume loss was determined by subtracting the final observed volume from the target volume. The missing volume was determined by subtracting the test volume loss from the total volume loss.

Peel and wedge tests were performed on specimens prepared using Boegel EPII after the individual ingredients were stored per the Navy shipping profile of 140°F. The purpose of this test is to demonstrate the components can withstand the test exposure and to provide a baseline for future kitting concepts.

Three ml each of GTMS, TPOZ, and GAA were placed into glass vials and stored in a 140°F oven for two weeks. The DI water was stored in a Nalgene bottle. Boegel-EPII was then made using stock chemicals and the conditioned chemicals using the test matrix in Table 4.4-6. Surfactant was not used in these tests.

Table 4.4-6 High Temp Conditioning 2-part Kit Matrix

ID No.	Ambient Condition	140°F Condition
1	DI H_2O + GTMS	TPOZ + GAA
2	DI H_2O + TPOZ + GAA	GTMS
3	DI H_2O	GTMS+ TPOZ + GAA
4	GTMS+ TPOZ + GAA	DI H_2O
5	DI H_2O + GTMS+ TPOZ + GAA	none

Aluminum alloy 2024-T3 bare adherends were used to prepare all test assemblies. The adherends were aqueous degreased and alkaline cleaned. The adherends were then abraded with Merit 180 grit aluminum resin bond (ALO) sandpaper on a random orbital sander. Boegel-EPII was brush applied within 30 minutes of abrasion. BR 6747-1 primer was spray applied and cured for 75 minutes at 250°F. Adherends were bonded using AF 163-2 OST adhesive and autoclave cured. Peel specimens were tested per BSS7206 Class 1 at ambient conditions.

Wedge test specimens were tested per ASTM D 3762 and exposed to environmental conditions of 140°F and 98% relative humidity. Wedge test results are presented in Table 4.4-7and Figure 4.4-10. Peel test results are presented in Table 4.4-8 and Figure 4.4-11.

Table 4.4-7 High-Temp Conditioning 2-Part Kit Wedge Data

ID No.	Ambient Condition	140°F Condition	Crack Length (inch) after Exposure to 140°F and > 98% RH (hours)						Crack Growth		% Coh Fail
			0	24	168	336	504	672	inch	St Dev	
1	H_2O / GTMS	TPOZ / GAA	1.17	1.30	1.41	1.42	1.42	1.42	0.25	0.03	90
2	H_2O / TPOZ / GAA	GTMS	1.16	1.30	1.40	1.42	1.42	1.42	0.26	0.03	91
3	H_2O	GTMS / TPOZ / GAA	1.15	1.29	1.40	1.41	1.41	1.41	0.26	0.02	91
4	GTMS / TPOZ / GAA	H_2O	1.13	1.26	1.35	1.37	1.37	1.37	0.24	0.05	92
5	H_2O / GTMS / TPOZ / GAA	none	1.15	1.29	1.34	1.37	1.36	1.36	0.21	0.04	94

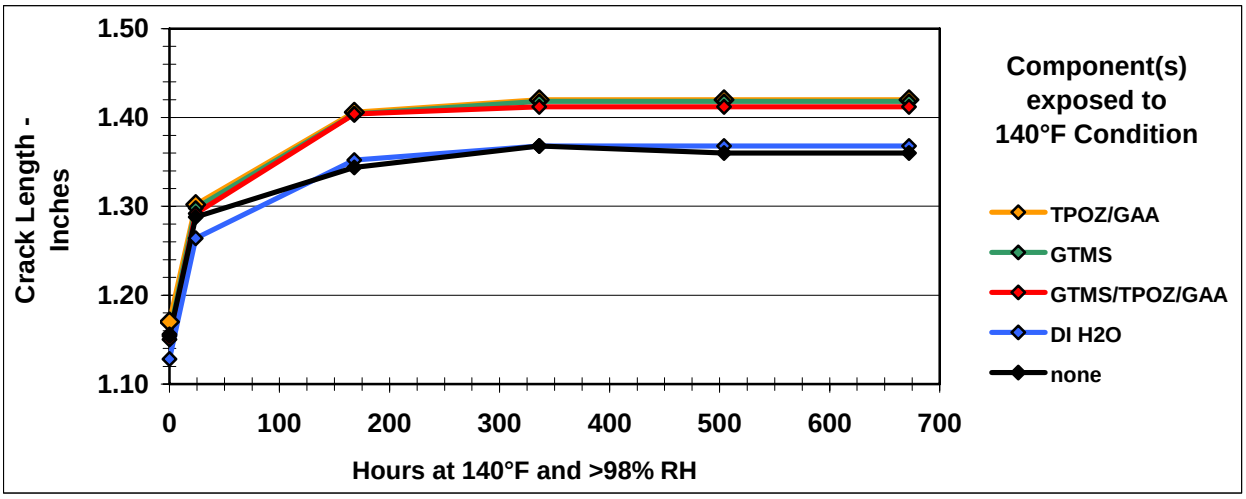


Figure 4.4-10 High temp conditioning wedge test crack extension

Table 4.4-8 High-Temp Conditioning Kit Peel Test Results

ID No.	Ambient Condition	140°F Condition	Peel Strength		% Coh Failure
			lbf/ in	St Dev	
1	H_2O / GTMS	TPOZ / GAA	81	6	100
2	H_2O / TPOZ / GAA	GTMS	83	3	100
3	H_2O	GTMS / TPOZ / GAA	83	3	100
4	GTMS / TPOZ / GAA	H_2O	81	4	100
5	H_2O / GTMS / TPOZ / GAA	none	82	5	100

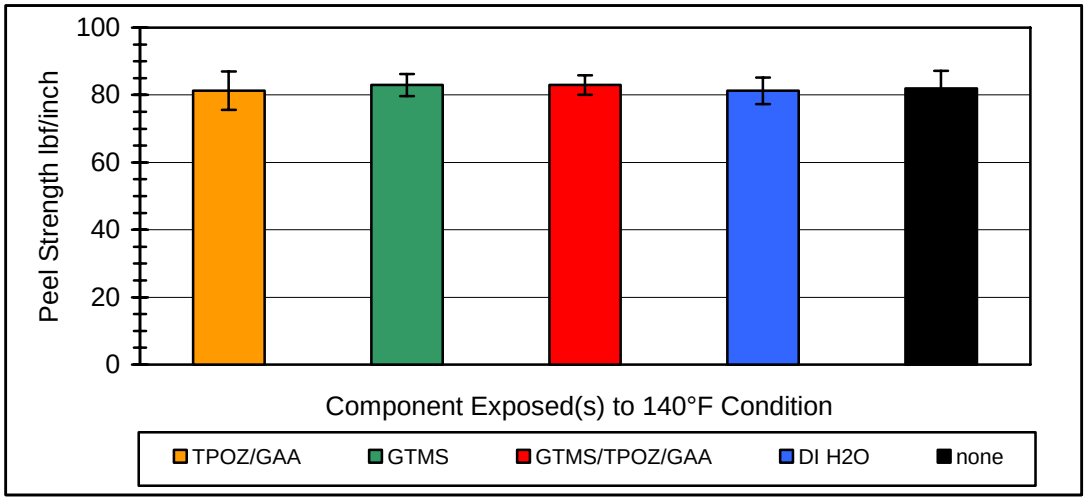
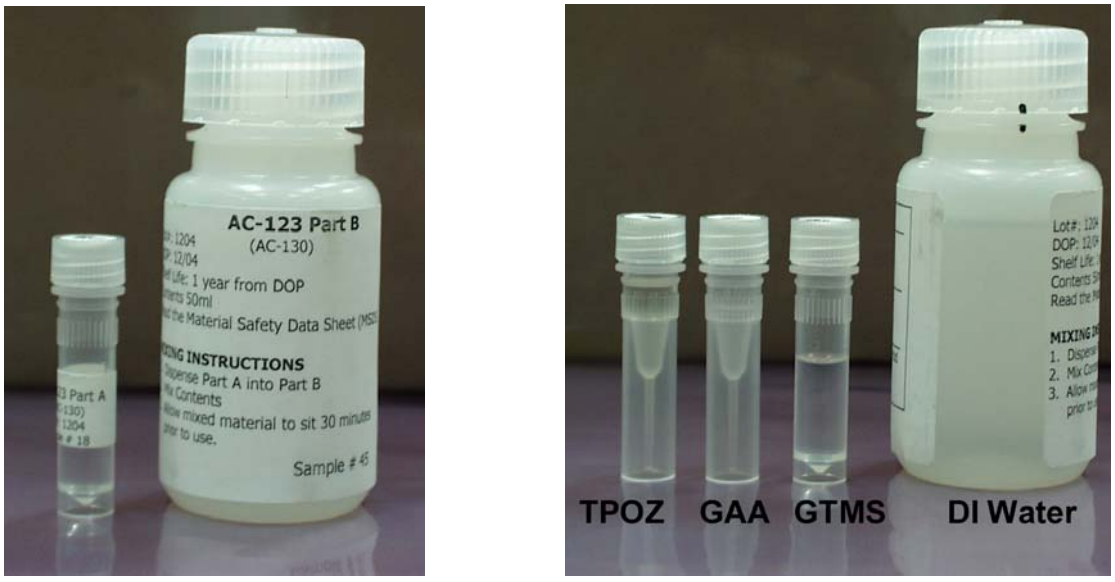


Figure 4.4-11 High-temp conditioning peel value comparison

The peel and wedge tests show no significant differences in the specimens that were treated with any of the heat-exposed sol-gel ingredients when compared with the control specimens.

4.4.4 Third-Generation 2-Park Kit Development: AC-130-2

In these tests, Boeing and AC Tech evaluated Nalgene Micro Packaging vials (Figure 4.4-12) as candidates for both the 4-part and 2-part AC130 kits.



2-part kit ***4-part kit***

Figure 4.4-12 Third-generation 2-Part Kits Using Nalgene micro packaging vials

As in previous storage stability testing, the 4-part kit components (GTMS, TPOZ and GAA) were subjected to standard conditions (77°F/50% RH), hot/wet conditions (100°F/95% RH or 95°F/85% RH), and hot/dry conditions (140°F oven). The 2-part kits were subjected to these conditions plus an additional condition of 2 weeks hot/dry (140°F oven) followed by exposure at standard conditions (77°F/50% RH) or hot/wet conditions (100°F/95% RH or 95°F/85% RH).

The vials were nitrogen flushed during filling and sealed in nitrogen-purged Mylar bags prior to environmental exposure. Only the active ingredients (GTMS, TPOZ, and GAA) were tested in the 4-part kits. The entire 2-part kit was evaluated. The 2-part kit consists of Part A (DI water, TPOZ, GAA and surfactant) and Part B (GTMS). The components evaluated were sized to make a 50 ml kit.

Weight loss results for 4-part kits are shown in Table 4.4-9 and Figure 4.4-13, where negative numbers indicate weight gain. GTMS was the most stable component, with losses less than 1% for all exposure conditions. The TPOZ had losses less than approximately 1% for the standard and hot/wet conditions; however, the losses were up to approximately 5% for the hot dry condition. Of the three components, the GAA showed the worst performance at each of the exposures, with losses greater than 10% for both 2 weeks at the hot/dry condition and 19 weeks at the hot/wet condition.

The magnitude of the TPOZ and GAA losses at the hot/dry condition (Navy shipping profile) are a concern because the mix ratio of the system is significantly impacted. The TPOZ component is dissolved in approximately 30% propanol, and it is not known if the weight loss is due primarily to solvent loss or loss of the zirconium component. Solutions made from the components stored

at these conditions appeared to mix normally, and wedge test and peel test results were also within normal parameters.

This problem may be avoided with the 2-part kit configuration, where the volatile GAA and the TPOZ are incorporated in the water component rather than packaged separately. Early weight loss results for the 2-part kit study, shown in Table 4.4-10 and Figure 4.4-14, indicate very small losses of Part A (GTMS) and Part B (aqueous solution) at the hot/dry storage condition as well as the standard storage condition.

Weight loss was determined for 19 week exposures for the 4-part kits and 12 week exposures for the 2-part kits. Analytical testing was conducted to determine the impact of storage conditions and weight loss on the performance of both the 4-part and 2-part kits. Gas chromatography and FT-IR results indicated little or no residue from the packaging in the bulk components as a function of exposure time or environmental condition. Performance tests are presented in Table 4.4-11 and Table 4.4-12 and Figure 4.4-15 - Figure 4.4-18.

Table 4.4-9 Weight Loss (%); Phase III 4-part Kit Storage Stability Study

Kit Exposure Condition	Data Source	TPOZ		GAA		GTMS	
		Avg.	Std. Dev.	Avg.	Std. Dev.	Avg.	Std. Dev.
Hot/dry	Boeing	4.64	1.26	14.20	0.91	0.84	0.06
2 week	AC Tech	2.50	0.18	10.88	0.08	0.49	0.09
Standard	Boeing	0.20	0.00	0.14	0.50	0.03	0.06
2 week	AC Tech	no data	no data	no data	no data	no data	no data
Standard	Boeing	0.00	0.20	-0.14	0.25	-0.06	0.28
4 week	AC Tech	-0.03	0.07	-0.19	0.17	0.03	0.02
Standard	Boeing	0.07	0.11	0.29	0.25	NA*	NA*
8 week	AC Tech	NA	NA	NA	NA	NA	NA
Standard	Boeing	NA	NA	NA	NA	NA*	NA*
12 week	AC Tech	0.18	0.11	1.69	0.81	0.03	0.04
Standard	Boeing	0.20	0.00	0.65	0.31	NA*	NA*
19 week	AC Tech	NA	NA	NA	NA	NA	NA
Standard	Boeing	0.20	0.00	0.87	0.00	NA*	NA*
33 week	AC Tech	NA	NA	NA	NA	NA	NA
Hot/Wet	Boeing	0.26	0.11	1.01	1.76	0.16	0.28
2 week	AC Tech	0.14	0.12	1.32	0.67	0.05	0.03
Hot/Wet	Boeing	0.33	0.11	2.03	0.25	0.06	0.28
4 week	AC Tech	0.38	0.13	2.96	0.38	-0.05	0.04
Hot/Wet	Boeing	1.37	1.36	4.20	0.50	-0.06	0.06
8 week	AC Tech	NA	NA	NA	NA	NA	NA
Hot/Wet	Boeing	NA	NA	NA	NA	NA	NA
12 week	AC Tech	1.03	0.13	5.79	0.51	0.41	0.26
Hot/Wet	Boeing	1.18	0.00	10.22	0.92	0.05	0.00
19 week	AC Tech	NA	NA	NA	NA	NA	NA
Hot/Wet	Boeing	1.76	0.00	17.83	1.84	0.10	0.14
33 week	AC Tech	NA	NA	NA	NA	NA	NA

* remaining supply of ambient temp storage samples of GTMS enclosed in Mylar® envelopes were utilized in the 2-part kit study.

Table 4.4-10 Weight Loss (%); 2-Part Phase III Kit Storage Stability Study

Kit Component and Exposure Condition	Total Exposure Time - Weeks			
	2	4	12	26
Part A: room temp	-0.00657	-0.09416	-0.13151	-0.13940
Part B: room temp	0.01133	0.01132	0.05468	0.04910
Part A: 95°F / 85%RH	0.04836	-0.09671	0.00000	0.14507
Part B: 95°F / 85%RH	0.03081	0.02969	0.09193	0.12418
Part A: 140°F	1.01547			
Part B: 140°F	0.38885			
Part A: 2 weeks @ 140°F + room temp		0.82205	0.72534	0.67698
Part B: 2 weeks @ 140°F + room temp		0.37900	0.41360	0.49494
Part A: 2 weeks @ 140°F + 95°F / 85%RH		0.82205	0.67698	0.82205
Part B: 2 weeks @ 140°F + 95°F / 85%RH		0.40208	0.42204	0.43351

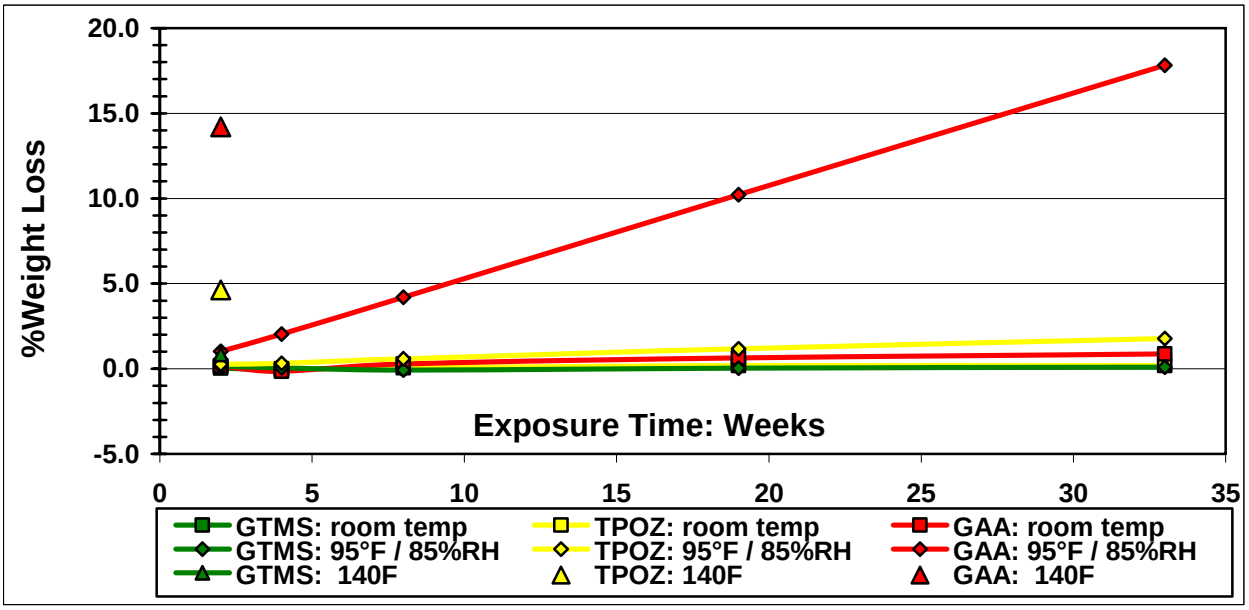


Figure 4.4-13 Percent weight loss of 4-part kit components for 3rd-generation kits

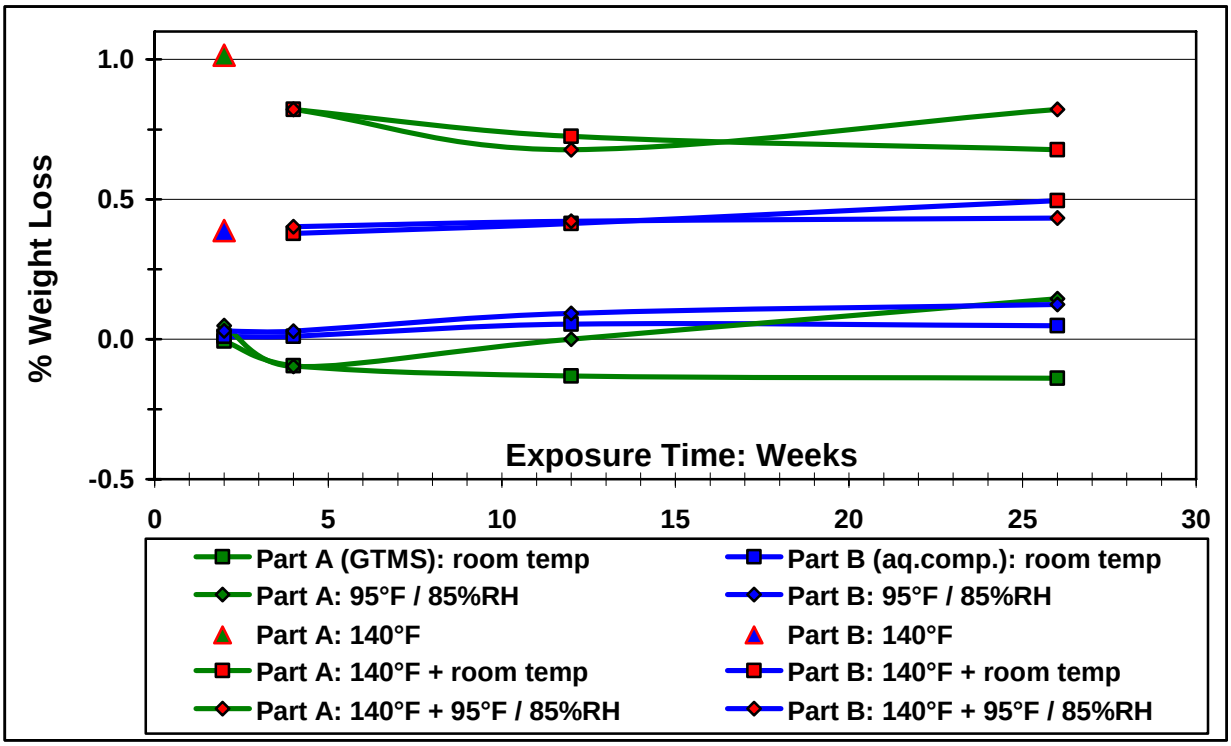


Figure 4.4-14 Percent weight loss of 2-part kit components in 3rd-generation kits

Table 4.4-11 Wedge Test Data for 3rd-Generation Kit Exposure Studies

Kit Exposure Condition	Crack Length (inch) after Exposure to 140°F and > 98% RH (hours)						Crack Growth		% Coh. Failure
	0	24	168	336	504	672	Total (inch)	Std. Dev.	
2 weeks 140°F	1.19	1.33	1.42	1.42	1.43	1.43	0.24	0.06	80
2 weeks H/W	1.19	1.35	1.45	1.45	1.48	1.48	0.30	0.08	69
2 weeks RT	1.12	1.28	1.36	1.36	1.38	1.39	0.27	0.03	69
4 weeks H/W	1.18	1.38	1.50	1.55	1.57	1.57	0.39	0.07	55
4 weeks RT	1.16	1.34	1.46	1.47	1.50	1.50	0.34	0.08	43
8 weeks H/W	1.19	1.38	1.49	1.51	1.56	1.59	0.40	0.08	75
8 weeks RT	1.21	1.36	1.47	1.51	1.56	1.59	0.38	0.07	78
19 weeks H/W	1.21	1.39	1.50	1.50	1.53	1.57	0.36	0.13	66
19 weeks RT	1.17	1.33	1.49	1.54	1.54	1.57	0.40	0.07	74
19 week Control: Boegel EPII	1.23	1.42	1.50	1.53	1.53	1.53	0.30	0.03	78

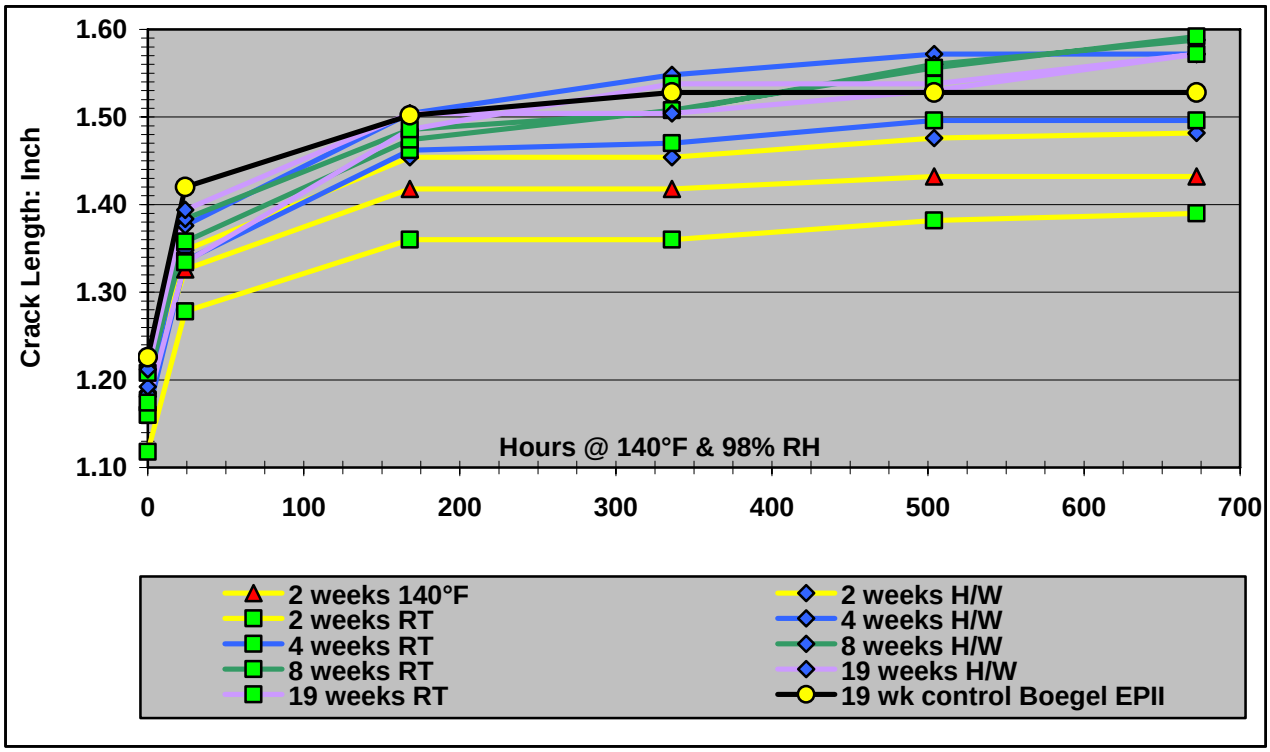


Figure 4.4-15 AC-130 4-part 3rd-generation kit wedge test results

Table 4.4-12 3rd-Generation 2-Part Kit Wedge Test Data

Kit Exposure Condition	Crack Length (inch) after Exposure to 140°F and > 98% RH (hours)						Crack Growth		% Coh. Failure
	0	24	168	336	504	672	Total (inch)	Std. Dev.	
14 days 140°F	1.15	1.28	1.42	1.48	1.52	1.55	0.39	0.04	92
14 days 95°F/85% RH (H/W)	1.16	1.35	1.46	1.46	1.51	1.55	0.39	0.03	88
14 days Room Temp (RT)	1.19	1.32	1.46	1.49	1.54	1.59	0.39	0.05	88
2 wk 140°F + 2 wk H/W	1.18	1.38	1.52	1.55	1.58	1.59	0.42	0.04	40
2 wk 140°F + 2 wk RT	1.19	1.40	1.54	1.58	1.58	1.62	0.42	0.04	50
4 weeks H/W	1.19	1.44	1.57	1.62	1.67	1.67	0.48	0.02	25
4 weeks RT	1.19	1.40	1.54	1.57	1.58	1.62	0.43	0.04	24
2 wk 140°F + 10 wk H/W	1.23	1.41	1.46	1.48	1.51	1.51	0.27	0.059	87
2 wk 140°F + 10 wk RT	1.25	1.42	1.48	1.54	1.54	1.54	0.29	0.041	80
12 weeks H/W	1.22	1.39	1.46	1.52	1.52	1.52	0.30	0.042	84
12 weeks RT	1.17	1.38	1.46	1.50	1.50	1.52	0.35	0.041	79
12 wk control Boegel EPII	1.23	1.42	1.50	1.53	1.53	1.53	0.30	0.026	78

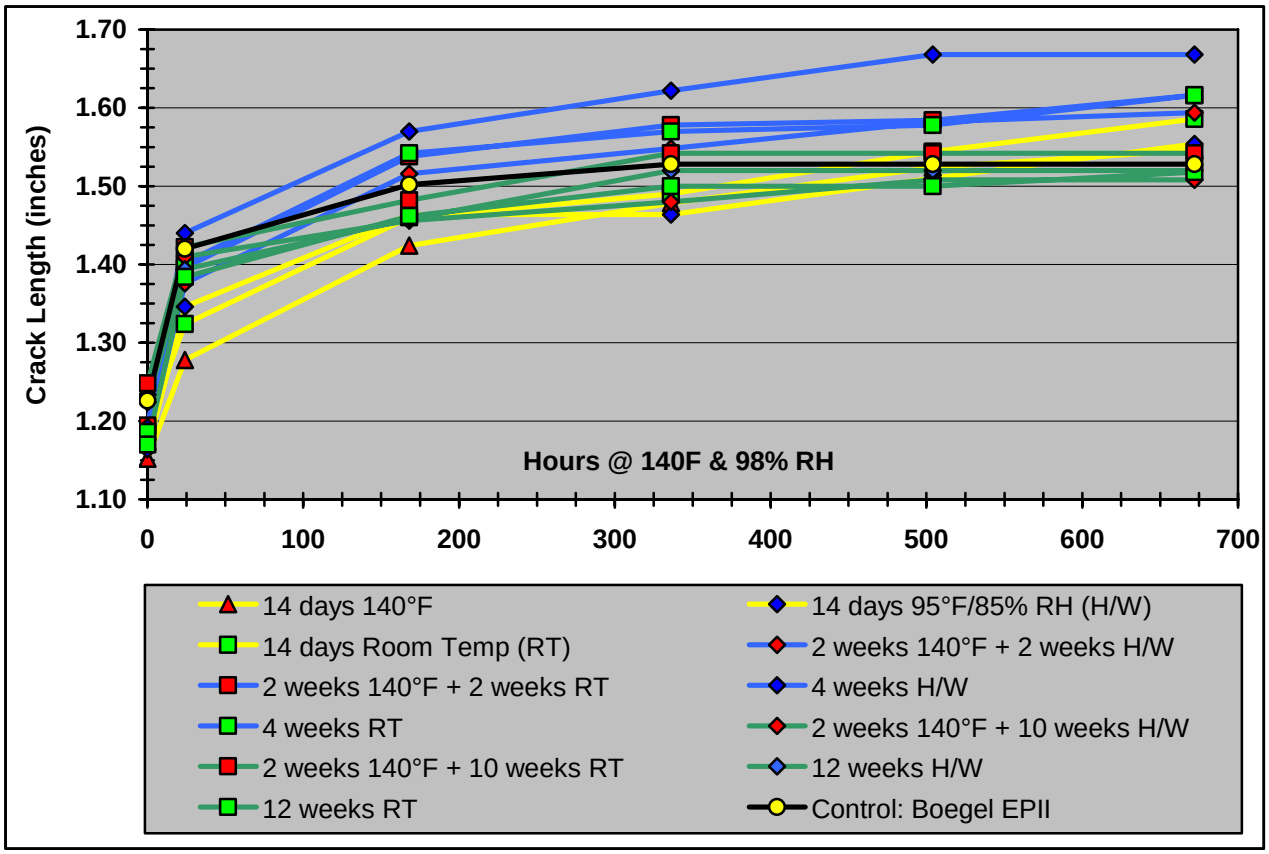


Figure 4.4-16 AC-130-2 3rd-generation 2-part kit wedge test results

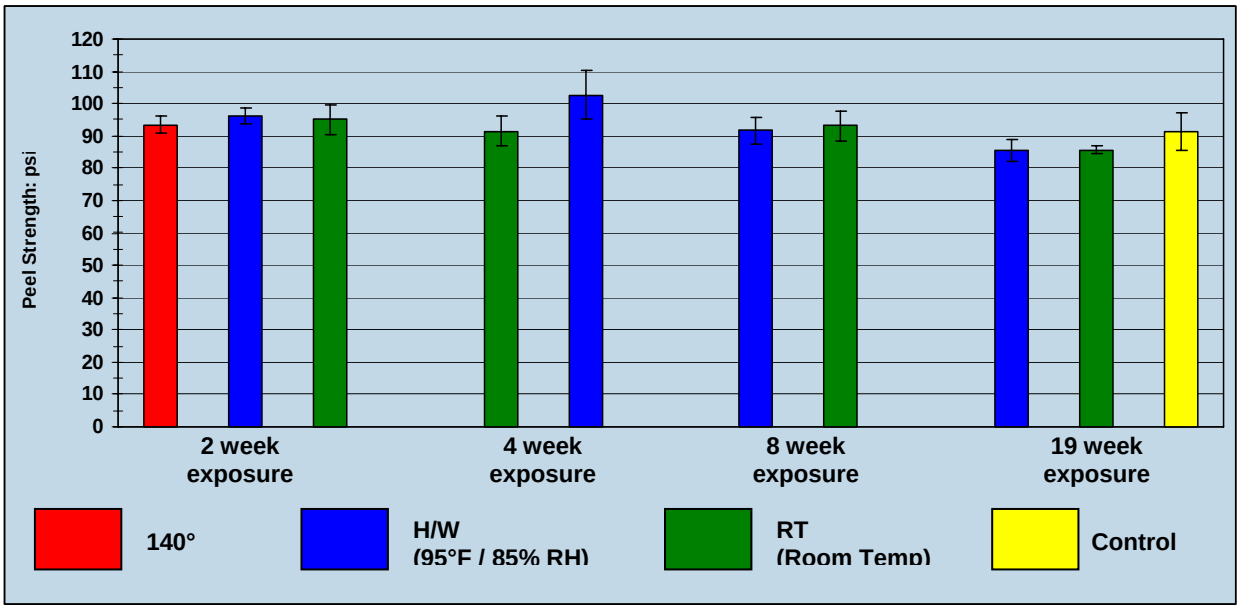


Figure 4.4-17 AC-130 3rd-generation 4-part kit peel test results

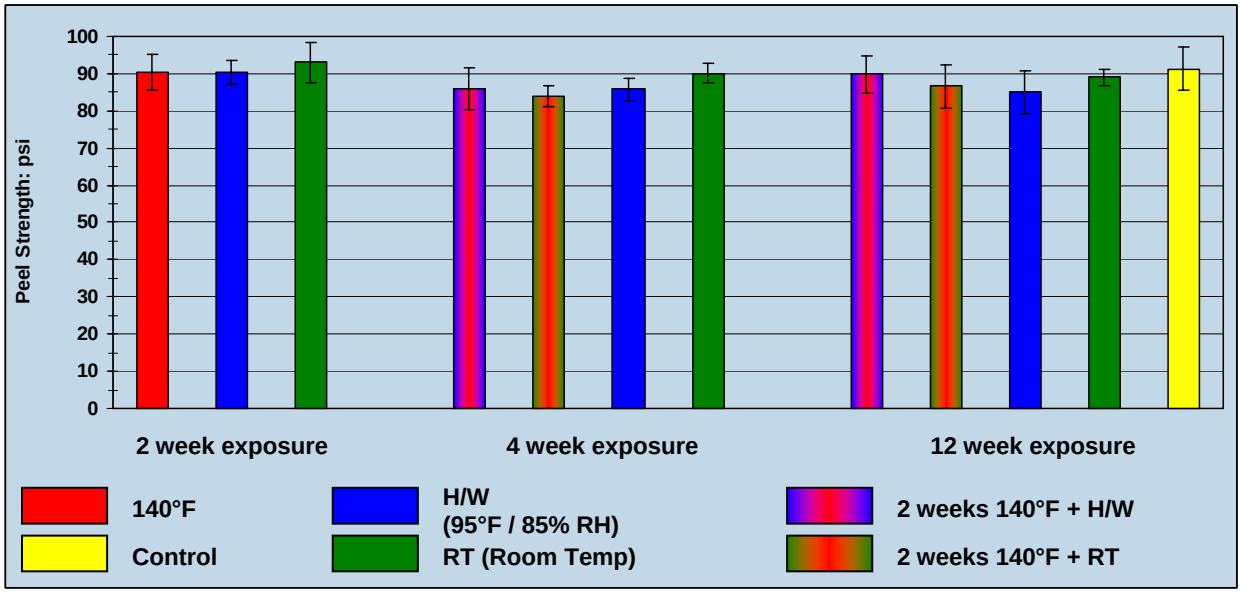


Figure 4.4-18 AC-130-2 3rd-generation 2-part kit peel test results

At first glance, the wedge test 2 week exposures for both the 2 and 4-part kits appeared to perform better than longer exposure times at all conditions. For the most part, the two week exposure kits showed a smaller initial crack length and crack growth and a greater percent cohesive failure than the longer exposed kits. There are several other factors to consider. The pretreatment used was the same one as used in the first generation 2-part kit: random orbital sanding on 2024-T3 aluminum substrates. This is not the most robust method but one that is more sensitive to differences in preparation. Other factors, such as age of the primer and adhesive also come into play. It should be noted specimens from a given exposure time perform similarly regardless of the exposure condition.

The 12 week 2-part kit and 19 week 4-part kit test specimens were all prepared at the same time along with a Boegel-EPII control specimen. This control was made fresh from laboratory stock chemicals. It is represented by the red line in Figure 4.4-15 and Figure 4.4-16. It is performing identically to the 12 and 19 week exposure test specimens to date. The test specimens will be broken apart and failure mode determined when the test is complete. The peel tests showed no differences between any exposure condition, length of exposure, number of kit components or control.

Testing of these kit configurations will continue after the conclusion of this project in order to assess the maximum shelf-life of these kit configurations.

5 Conclusions

Overall, confirmation of the robustness and durability of the Boegel-EPII system for use as a surface preparation technique on metal alloys was achieved. Several conclusions were noted

Deoxidation Methods: Studies indicate careful choice of abrasive media and tools is required to achieve reproducible performance for the surface preparation of aluminum alloys. Verification of these processes and expansion of the processing guidelines were determined under this effort. An abrasive paper was identified that gives reproducible performance under a variety of conditions. This paper and process was included in baseline procedures. Second source abrasive papers were identified, and their performance continues to be verified. The same abrasives may also be used effectively on titanium alloy substrates.

Alternatively, chemical deoxidation methods that give good performance were identified for parts and hardware that cannot use abrasive methods. The best-performing methods on aluminum used a mild alkaline conditioner with or without an additional acid desmut. The use of an open air plasma process may improve the surface cleanliness, but the results were not conclusive.

Primer Cure Methods: Minimum cure times and temperatures were identified for parts that cannot tolerate an extensive heat cure cycle. Data indicate a minimum of 200°F was necessary to reproducibly cure the primer using a heat blanket under vacuum bag conditions. Cocuring of the primer with different adhesive systems was evaluated to determine the compatibility of the primer with the adhesive chemistries. Significant differences could be seen between adhesives. Alternative environmentally-compliant bond primers were evaluated for use with the Boegel-EPII system. Only the Cytec BR 6747-1 series and the SIA AL2000 products showed acceptable performance with the Boegel-EPII system.

Packaging Methods: Extensive kitting and packaging evaluations were conducted eventually resulting in a packaging system that shows the durability and resistance to storage conditions required for use in production and repair setting.

Transition Opportunities: Transition of materials and processing information and support of transition efforts to specific customers was provided throughout the effort Procedures were documented specifying all of the preferred materials and processes.

6 References

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